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tests. Undiluted, the Additive is toxic by inhalation and moderately toxic dermally.[18]/[19]/[20]/[21]/[22]/[23]/[24]/[25]/ However, once blended with gasoline at recommended concentrations, there is no risk of intoxication from the normal handling or use of gasoline.

The OSHA permissible exposure limit and the ACGIH threshold limit value for the Additive (MMT) is 200 ug manganese/m^3. Workplace exposures are typically less than 100 ug manganese/m^3

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and refinery concentrations less than 10 ug manganese/m^3. Of note, the Additive was not detected in ambient air at several locations at street level in Toronto at a limit of detection of 0.00005 ug/m^3.[26]

The Additive presents no hazard to public health from use in gasoline. Because of the very low concentration at which the Additive would be used in gasoline, 0.031 gm manganese/gal (8 mg manganese/1), its low vapor pressure (0.05 mm Hg at 20°C), its decomposition in sunlight in seconds, and its almost complete combustion in the engine,[27] use of the Additive poses no hazard to the public.

IV. **CONCLUSION**

The use of the Additive as a fuel additive poses no public health concerns from the standpoint of exposure to increased ambient concentrations of manganese, ambient concentrations of the Additive, or as a result of direct exposure to the Additive.

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Manganese in Air in Ontario, Canada

Area	Concentration (ug/m^3) by Year					
	1982	1983	1984	1985	1986	1987
Overall	0.041	0.043	0.049	0.060	0.046	0.054
Toronto	0.027	0.026	0.030	0.041	0.027	0.045
Hamilton	0.113	0.117	0.145	0.147	0.154	0.137
Cities 100,000 - 500,000						
All	0.060	0.061	0.075	0.085	0.065	0.071
Without major point source	0.027	0.029	0.033	0.050	0.034	0.042
Towns 30,000 - 100,000						
All	0.045	0.049	0.046	0.064	0.036	0.042
Without major point sources	0.015	0.015	0.013	0.023	0.010	0.020
Towns less than 30,000						
All	0.010*	0.020*	0.024*	0.021*	0.015*	0.032*
Without major point sources	0.010*	0.020*	0.024*	0.021*	0.012*	0.020*

* No manganese in air values were reported for cities
  with point sources and population less than 30,000
  from 1982-85. Windham was added in 1986 and Nanticoke
  1987.

Appendix 9

APPENDIX 9

COMPILATION OF SCIENTIFIC STUDIES THAT PROVIDE
ADDITIONAL SUPPORT FOR THE
HiTEC 3000 ADDITIVE WAIVER APPLICATION

"AN INVESTIGATION OF THE EFFECTS OF GASOLINE COMPOSITION AND VEHICLE SYSTEMS ON EXHAUST EMISSIONS"

Joseph M. Colucci
General Motors Research Laboratories

Presented to
CRC Automotive and APRAC Committees
June 20, 1989

REVISED June 21, 1989

MEETING OBJECTIVES

To propose, review and discuss a CRC program to evaluate the effects of changes in gasoline composition on vehicle exhaust emissions.

Specifically, we need to:

    a) Agree on objective for program

    b) Agree on major elements in program

    c) Agree to have a small task force develop and cost a program

PROGRAM OBJECTIVE*

To investigate the potential of changing gasoline composition to reduce vehicle exhaust emissions in the 1990's and beyond. Specifically, measurements will be made of

- Regulated emissions (HC, CO, NO$_x$) which impact ozone and carbon monoxide pollution, and

- Unregulated emissions which can impact ozone pollution and greenhouse gases

The program will utilize production vehicles representative of the engine-emission control systems expected to prevail in the 1990's.

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*NOTE: This covers Part I, A & B, of the overall research program plan, as described on the next page

Overall Research Program Plan

Part I - To be completed by July 1990

A) Investigate the impacts on exhaust emissions of changes in gasoline composition. 1989 and 1990 model (if available when needed) vehicles, and variable and flexible fueled vehicles, representing the latest engine-emission control system technologies will be used to represent the vehicle population of the 1990's. All emission tests at 75°F, and all fuels at 9 RVP. The VFV's, FFV's, and GTMV's will be tested with M-85 as well as with other test fuels.

B) If Part A demonstrates that gasoline composition changes reduce exhaust emissions, a similar program will be carried out with earlier model year vehicles that will be in the vehicle population in the 1990's

Part II - To be run contingent on results from Part I.

Projects will be considered to cover the following subjects:

A) Driveability

B) Non-exhaust emissions (including variations in RVP)

C) Durability

D) Atmospheric modeling

E) Emission tests at non-standard temperatures

F) Impacts of aromatic and olefin type

G) Future emission control technologies

A, B, C, E and G would utilize the "low emissions gasolines" from Part I. D would utilize the results from the exhaust gas speciation measurements from Part I.

WHY IS THE PROGRAM NECESSARY?

- _Nationwide interest in cleaner air_

  - _Bush administration proposals_

  - _Revised Clean Air Act_

  - _California and SCAQMD proposals_

  - _Fuel receiving considerable attention_

- _Improved gasoline could be beneficial to petroleum and automotive industries_

  - _Minimizes changes in fuel infrastructure to reduce emissions (compared with shift to alternative-non petroleum based-fuels)_

  - _Supplements changes in vehicles to reduce emissions_

  - _Could be a lower cost and more rapidly implemented means for improving air quality than alternative fuels_

  - _Could provide more time to develop vehicles and the infrastructure needed for alternative fuels_

MAJOR PROGRAM ELEMENTS

- Vehicles - Representative of the population that will exist in the 1990's

    - Production vehicles only

    - Emphasis on latest models

- Fuels - Gasolines

    - Gasoline ether blends

- Measurements - Exhaust emissions (tailpipe, engine out, modal)

    - FTP at sea level (75°F)

    - Regulated emissions (HC, CO, NO_x)

    - Unregulated emissions (CO_2, CH_4, Aldehydes, Speciation)

    - Fuel economy (MPG, MPBTU)

    - Effect of fuel change after some mileage accumulation on test fuel (ECM learning also)

- Statistically-designed experiment

- Contract study

- Funding

<u>VEHICLES</u>

Must represent different engine-emission control system technologies. Number to be decided.

- Half 1989 and 1990 (if available when needed) models
  (Most representative of vehicles in 1990's)

- Half to cover remainder of vehicles
  (1982-1988 models)

- Distributed to represent
  - Sales distribution (GM, Ford, Chrysler, Foreign*)
  - Fuel systems (PFI, TBI)
  - Engines (4-, 6-, 8-cylinder)
  - Technologies (2- and 4- valve; knock sensors; compression ratios; etc.)
  - Emission control systems (catalytic converters; computer controls)

- Can be rental or purchased cars

- Should have break-in mileage (10,000 miles minimum)

- Should be properly operating
  - According to manufacturers specs
  - Meeting applicable emissions standards

- Could include VFV's, FFV's, and GTMV's tested on M-85 and improved gasolines

*Include only if AIA provides financial and technical support for program.

FUELS

- A matrix based on table below

Factor	MVMA Survey Range	Proposed Levels Low	High
Aromatics, %	12 - 54	15	45
Oxygenates, % O2	0 - 4.6	0	3.7
Sulfur, %	0 - 0.15	0.001	0.03
90% Dist. Temp., °F	276 - 409	280	370
Olefins, %	1 - 37	2	30

Notes:

- Normal refinery components

- Ethers preferred for oxygenates (ETBE, MTBE)

- Oxidation inhibitors

- A common, representative deposit control additive

- All fuels at 9 RVP (summer gasoline)

- Octane quality (R+M)/2 = 87 min.

- Indolene is baseline fuel

- Aromatic and olefin reductions should maintain same relative concentrations of specific components

EFFECT OF GASOLINE AROMATIC CONTENT ON TAILPIPE EMISSIONS*

Fuel: % A 90%, °F		49%** 376 (2 tests)	Howell EEE 31%** 306 (3 tests)	13%** 277 (2 tests)	% Decrease 49 -> 13
	HC	0.79	0.58	0.49	38
Emissions g/mile	CO	6.08	4.77	3.81	37
	NOx	0.63	0.54	0.42	33
Fuel Economy	MPG	19.0	18.2	17.7	6.8
	MPG/ Density	24.6	24.9	25.1	(-2.0)

* 1987 Olds Ciera, 2.8L, V-6 engine with ~50,000 miles

** Remainder Paraffins (1% olefins in EEE)

EFFECT OF GASOLINE SULFUR CONTENT ON TAILPIPE EXHAUST EMISSIONS

	Emissions - g/ml		Percent Decrease
	0.030% S*	0.004% S**	
HC	0.17	0.16	6
CO	1.42	1.06	25
NOx	0.31	0.26	16

* Sulfur compounds added to EEE

** Base fuel = Howell EEE

Emissions values are averages for four repeat tests.

1989 Buick LeSabre, 3.8L, V-6 engine, ~2,500 miles

EFFECT OF FUEL COMPOSITION ON OCTANE QUALITY AND CO_2 EMISSIONS

Fuel	Octane, (R+M)/2	CO_2 Emissions, grams/MJ
High-aromatic gasoline (49A)	92.3	76.4
Low-aromatic gasoline (13A)	85.6	71.6
Low-aromatic + 25% ETBE	92.4	66.2*
Percent decrease (49A -> 13A + 25 ETBE)		13

* Assumes that the ethanol used to produce ethyl tertiary-butyl ether (ETBE) is derived from biomass.

PROPOSED EXPERIMENTAL DESIGN

- *Include a statistical consultant*

- *Explore "fuel" and "engine-emission control system" variables*

- *Minimum of duplicate tests per fuel-vehicle combination*

To determine fleet size, must decide on:

- *Magnitude of difference in each constituent (HC, CO, NO_x, CO_2, MPG) we wish to detect*

- *Confidence level in detecting that difference*

- *Estimate of test variance for each constituent and for vehicles*

Consider using engine-out measurements in determining statistical requirements

CONTRACT STUDY

- *Single contractor best for emissions work*

- *Program manager to be hired by CRC*

PARTICIPANTS AND FUNDING SOURCES

- Necessary

    - API and MVMA
        (Program will require special funding and high
        priority)
    - EPA and CARB*

- Optional

    - Import Car Association (AIA)

*Contacts should be made at high levels of auto and petroleum
companies.

THE ROLE OF ETHERS

IN LOW-EMISSION GASOLINE

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OCTOBER 3-5, 1989

The Role of Ethers in "Low Emission" Gasoline

Abstract

The reformulation of gasoline is once again being proposed to make it a cleaner burning fuel that will reduce the emission of pollutants from the automobile. This time the petroleum industry has a better chance of attaining that goal. Unlike the 70's and the early 80's, the path is not being clouded with energy crisis or lead phase out issues. Of course, the refiners also now have an effective tool that was not available back then, and that tool is the fuel ethers such as MTBE. The ethers are expected to be a key ingredient in the production of the "low emission" gasoline of the future.

INTRODUCTION

The large scale reformulating of gasoline for the purpose of reducing ozone forming emissions from automobiles was first proposed by General Motors in 1972 (1). However, the ensuing energy crisis of 1973 overrode any national concern to clean the environment by modifying gasoline composition. The combination of pressures from gasoline shortages and the phase out of lead put the concept of improving the environmental quality of gasoline on the back burner while coincidentally creating an increase in more environmental problematic constituents of gasoline.

As more fluid cat crackers were built to increase gasoline yield, it also increased the production of the atmospherically reactive light olefins. Increasing supplies of butane also allowed the refiner to further increase his gasoline yield by maximizing the vapor pressure (RVP) of the gasoline. Lastly, the production of aromatics from reforming was the most popular octane replacement for lead. However, the combustion products from aromatics seem to be more difficult for the emission control systems of today's car to handle. Now that the energy crisis and lead removal hurdles appear to be behind us, gasoline reformulation to reduce ozone forming emissions from automobiles is again being proposed. The question that now is being studied is which reformulation provides the greatest benefits at the least cost.

Though fuel oxygenates first became popular as an octane replacement for lead in gasoline, they are now recognized for their ability to control carbon monoxide emissions from automobiles as evidenced by the number of local oxygen mandates being implemented around the nation. Methyl tertiary butyl ether (MTBE) has been a major contributor to those clean air programs. Now it appears that MTBE and the other ethers will also be a key ingredient in allowing the refiner to make "low emission" gasoline for the high ozone/smog areas around the country. Not only do the ethers provide low volatility oxygen for leaning out the combustion process, but their high octane provides an ideal octane alternative to substitute for aromatics in the gasoline. The installation of a refinery ether unit has an added benefit since it also provides a very cost effective disposal for some of the more atmospherically reactive olefins that are currently blended into gasoline.

Though other refinery investments must also be made to expand production capability of "low emission" gasoline, the fuel ethers will be a main ingredient in the new formulation.

ENVIRONMENTAL QUALITIES

The most direct way to reduce the ozone contributing characteristics of gasoline is to undo many of the changes

that have occurred to gasoline over the past two decades by
lowering volatility and reducing the concentration of
aromatics and volatile olefins. The U.S. Environmental
Protection Agency (EPA) has already corrected some of these
unfavorable changes by implementing summertime RVP controls
that will reduce the amount of butanes being vaporized into
the atmosphere. Reducing aromatics and light olefins is much
more difficult, particularly without the use of leaded octane
enhancers.

The effect of aromatics and gasoline composition on exhaust
emissions had been studied many times before with the
pre-catalyst technology cars (2-4). These earlier studies
concluded that increasing gasoline's aromatic concentration
did not contribute to significantly higher amounts of
hydrocarbons in the engine out exhaust. It did, however,
swing the composition of the exhaust hydrocarbons toward the
higher molecular weight aromatics, and away from the lower
molecular weight olefins typical of the non-aromatic fuels.
One of these studies also looked at the effect on NOX
emissions (4). The results showed that aromatics in the fuel
significantly increased the amount of NOX in the exhaust. The
conclusion is that NOX production is a Time-Temperature
phenomenon, and that the aromatics with their high carbon
content have high combustion temperatures that increase the
production of NOX.

To further investigate fuel composition effects with newer car
fuel system technologies, FTP emission tests were conducted on
two port fuel injection cars (1985 Camaro and 1986 Honda).
Four fuels of varying aromatics concentration but similar
RVPs (8.5-9.5 psi) were used in the study. A intermediate
aromatic fuel in this study was indolene. The average changes
in exhaust emissions relative to indolene are illustrated in
Figure 1. As expected, the higher aromatic concentrations
lead to higher NOX emissions. Surprisingly, the other two
regulated exhaust emissions (HC & CO) also increased
significantly with increasing aromatic concentration. From
this data, it appears that the newer fuel system technologies
can handle the non-aromatic compounds much more easily than
the aromatic compounds.

These results suggest that reducing the aromatic content of
gasoline can make significant improvements in the cars'
exhaust emissions relative to their ozone forming tendency.
This seems to be consistent with results reported in General
Motors study (5-6). The only problem now is to find cleaner
burning substitutes for the high octane aromatics in gasoline.

OXYGENATES

The use of oxygenates in fuel is now a well accepted practice
to control CO emissions. However, when strategies were being

formulated to reduce ozone forming pollutants from mobile sources, the emission reducing potential of the oxygenate blends appears to have been overlooked by government agencies.

However, the available data suggest that blending oxygenates into gasoline can produce a significant reduction in unburned hydrocarbons in the tailpipe exhaust. The results in Figure 2 are based on the compilation of the data from 116 emissions runs reported in the literature for cars with catalytic converters. The data were also limited to emission studies in which the cars were tested on fuels with both low and high oxygen levels besides the base fuel. With these cars, the maximum reduction in exhaust hydrocarbons (approximately 10%) occurred with the lower oxygen level fuels, which averaged about 2% in this database. The fuels in these lab studies were essentially prepared by splash blending the hydrocarbon base fuel with the oxygenate. In some cases, the oxygenated test fuels are RVP corrected (or matched) by adjusting the butane content. However, none of these studies used test fuels that were matched on both RVP and octanes, which is the actual practice in the gasoline blending operations in the refinery. Therefore, these studies do not capture the additional emission benefit realized when the high octane oxygenates are used to selectively displace the high octane aromatics during the gasoline blending process at the refinery. The only oxygenate application that doesn't benefit from this refinery octane balancing operation is the gasohol topping of ethanol at the terminal.

To the best of our knowledge, no studies have been conducted that try to capture all the combined emission effects from blending just oxygenates in the refinery. However, the effect can be estimated by combining the data from Figure 1 and Figure 2. The estimated emission benefit realized when blending an ether at the refinery is illustrated in Figures 3A & 3B. The dashed lines represents the oxygenate effect while the solid lines include the additional benefit from reducing the aromatic content when the octane is kept constant. The analysis indicates that the optimum emission benefit from blending the ether appears to occur near the 2 % oxygen level in gasoline except for CO, which realizes some additional, but quickly diminishing, CO reduction from higher oxygen levels. Therefore, it appears that the emission reduction benefit from oxygenates is further enhanced when the oxygenates are blended at the refinery.

FUEL ETHERS

The best known fuel ether is MTBE which is produced by combining methanol with isobutylene. However, there are a number of other possible ethers that can be produced by combining various alcohols with olefins having the active tertiary carbons. One that is currently produced in limited

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amounts is Tertiary Amyl Methyl Ether (TAME) which is made by combining methanol with isoamylenes (2-methyl butenes). Another possible ether is Ethyl Tertiary Butyl Ether (ETBE) which is produced by combining isobutylene with ethanol instead of methanol. The ethanol analog for TAME is ETAE (Ethyl Tertiary Amyl Ether). The volume yield equations for these ethers are shown in Table 1 and their properties (except ETAE) are shown in Table 2.

The production technology and supply potential for these ethers are discussed in much greater detail in a number of previous papers(6-8). However, it is estimated that another 100 MBPD of MTBE and 100 MBPD of TAME can potentially be made from U.S. refinery process streams that contain the active olefins. This does not include the potential MTBE that can be produced with the commercial technology for converting butanes to MTBE.

ATMOSPHERIC REACTIVITY

Another major source of hydrocarbon emissions from vehicles are evaporatives which are emitted during the diurnal, hot soak and operating (running losses) modes of the vehicle. Unlike the tailpipe hydrocarbons, which are mainly made up of highly reactive compounds, evaporatives are made up of a number of hydrocarbon compounds of varying reactivity. As an example, Table 3 lists a number of the compounds that may be found in the gasoline-related emissions from cars. Also included are the blending vapor pressures and a measure of their atmospheric reactivity. The paraffins as a class are the least reactive hydrocarbons. On the other hand, the olefins are at least an order of magnitude more reactive than the paraffins. Aromatics tend to lie somewhere in between the two. Oxygenates, however, are also very low in reactivity.

In addition to reactivity, the blending vapor pressure of the compounds is also an important property since it is an indicator of the compound's tendency to evaporate from the gasoline. If a compound is not volatile enough to evaporate from the gasoline, it does not matter very much how atmospherically reactive it is. The importance of this relationship is best illustrated in Figure 4 where the reactivities of the compounds are cross plotted against their blending vapor pressure.

A letter code is used to represent the various chemical classes of compounds on this figure. Also, an envelope is draw around the area that represents compound properties with the worse ozone forming characteristics: high volatility and high reactivity. From this figure, it becomes obvious that only the volatile olefins fall into this area, and therefore, will likely contribute the most to the reactivity of the evaporative emissions. This is consistent with work reported

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by Ford Motors (7). Using actual vapor compositions from
gasoline refueling emissions, their calculations showed that
the olefins in the vapors can easily represent more than 50%
of the vapor's atmospheric reactivity even though the olefins
represent less than 10% of the hydrocarbon vapors. Earlier
work by Phillips observed similar results (8).

Based on the analysis in Figure 4, it appears that the fuel
oxygenates in general do not contribute much to ozone
formation in the gasoline vapors because of their
exceptionally low reactivity, and in the case of ethers, their
volatility. In fact, use of oxygenates at high levels in the
gasoline pool should lead to lower reactive vapors by diluting
the use of the more reactive hydrocarbon blendstocks produced
in the refinery. This analysis also implies that much of the
ozone forming tendency of gasoline vapors can be reduced by
removing the volatile olefins from the gasoline.

REFORMULATION FOR LOWER EMISSIONS

The previous analysis suggest reformulating gasoline can make
significant strides in reducing the ozone contributing
qualities of gasoline as well as the CO emissions from the
tailpipe. This can be done by removing some of the
environmentally less favorable components from gasoline and
replacing them with much cleaner burning components. There is
not enough information available yet to develop the best
formulation, but the available data do provide some direction.
These data imply the following reformulation strategies:

1. Reduce tailpipe emissions

   - maximize production or use of non aromatic octane
        components to reduce aromatic content

   - add low volatility oxygenate to lean out combustion

2. Reduce evaporative emissions and atmospheric reactivity

   - lower Reid Vapor Pressure

   - convert C4 and C5 olefins to saturated hydrocarbons

   - dilute remaining reactives with non-reactive
        blendstocks

Production of aromatics in the refinery can be minimized by
lowering reforming severity to 90-91 RON. At this severity,
the predominate reaction is only dehydrogenation of the
naphthenes, and very little paraffin is being converted to
aromatics. What this requires is the maximum production or
use of high octane non-aromatic components. Some of the
under-utilized but available refinery process technologies

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that help achieve this goal are C5/C6 isom with recycle for total conversion, alkylation of C5 olefins, and etherization of isobutylenes and isoamylenes.

The alkylation and ether units provide another environmental quality improvement by converting the atmospherically reactive C5 olefins into low volatility saturated blend stocks. In addition, an ether unit provide low volatility oxygenate in the form of MTBE and TAME if methanol is used, or ETBE and ETAE if ethanol is used.

ROLE OF ETHERS

In the development of "low emission" gasoline, the use of ethers provides many advantages to the point that it is likely to be the key ingredient in producing this gasoline. One key property of the ethers is that they provide low volatility oxygen for leaning out the combustion process to promote cleaner burning without increasing gasoline volatility. Another key property is the exceptionally high octane that allows them to be used for displacing aromatics in gasoline. And since the ethers are considered fungible gasoline blendstocks, there are no restrictions on the distribution of the finished gasoline product.

Refinery ether units provide an added advantage in that they convert very volatile and atmospherically reactive olefins into low volatility and cleaner burning oxygenates. So this process provides a very beneficial way of removing some of the light olefins from the gasoline pool.

Since feedstocks for refinery ether units are limited, supplemental ether supplies from outside sources will be required to achieve the maximum environmental benefit. This requirement is being satisfied by a growing number of MTBE operations that convert butane to MTBE. Using this MTBE also helps further dilute the concentration of the reactive compounds in the finished gasoline.

For all the above reason, the exceptional properties of ethers will provide the refinery with the flexibility to maximize his production of "low emission" gasoline.

LOW EMISSION GASOLINE

As previously mentioned, there is not enough information to determine the best formulation for making "low emission" gasoline. This information will probably be developed within the next year. However, from the previous discussions, there is enough information to speculate what the final gasoline

specification may be. Within the guidelines developed in this paper, this gasoline will have lower volatility, lower aromatics, and lower concentrations of volatile olefins than today's gasolines. It will also contain some oxygen. Therefore, gasoline specifications to reduce ozone related emissions may eventually look like those listed in Table 4.

CONCLUSION

Due to the building pressures to clean up the air in a number areas in the country, the refining industry will likely be reformulating gasoline to reduce emissions associated with the formation of ozone. Though many changes will be required, a key ingredient to achieving this goal will be the use of ethers such as MTBE.

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TABLE   1

VOLUME YIELD EQUATIONS FOR ETHERS

1.0 IC4= + 0.43 MEOH = 1.27 MTBE

1.0 IC4= + 0.62 ETOH = 1.46 ETBE

1.0 2MB= + 0.38 MEOH = 1.25 TAME

1.0 2MB= + 0.55 ETOH = 1.44 ETAE

NOTE: 2MB= ARE 2-METHYL BUTENES (ISOAMYLENES)

TABLE 2

FUEL ETHERS

GASOLINE RELATED PROPERTIES

	MTBE	ETBE	TAME
OCTANES:			
BLENDING RON	118	119	112
BLENDING MON	102	103	99
BLENDING (R+M)/2	110	111	105.5
BLENDING RVP (PSI)	8	4	1
BOILING PT. (F)	131	161	187
DENSITY (LB/GAL @60F)	6.2	6.2	6.4
WATER SOLUBILITY (WT%):			
WATER IN FUEL	1.4	0.5	0.6
FUEL IN WATER	4.3	1.2	1.15
MAX. CONCENTRATION (VOL%)	15.0	12.7	12.4
MAX. OXYGEN (WT%)	2.7	2.0	2.0

TABLES 3

ATMOSPHERIC REACTIVITY
VOLATILE GASOLINE & TAILPIPE EMISSION COMPOUNDS

HYDROCARBON TYPE	COMPOUND NAME	ATMOSPHERIC REACTIVITY (-OH RATE)	BLENDING VAPOR PRESSURE PSI
XX	METHANOL	1.0	60.0
XX	T-BUTANOL	1.1	11.0
P	Propane	1.2	190.0
A	Benzene	1.3	3.2
P	Isobutane	2.5	75.0
XX	MTBE	2.6	8.0
P	N-butane	2.7	55.0
XX	ETHANOL	3.4	18.0
P	Isopentane	3.6	21.0
P	N-pentane	5.0	16.0
P	Isohexane	5.0	6.8
P	N-hexane	5.6	5.0
A	Toluene	6.4	1.0
P	N-heptane	7.3	1.6
O	Ethylene	8	250.0
A	P-xylene	11	0.3
XX	FORMALDEHYDE	11	60.0
O	Propylene	17	226.0
A	M-xylene	23	0.3
O	Pentene-1	30	19.5
O	Butene-1	30	65.0
O	3M1butene	32	27.0
O	Hexene-1	36	6.0
O	Isobutene (1)	55	66.0
O	Butene-2	65	49.0
O	Pentene-2	68	15.5
O	2M1butene (2)	70	19.0
O	2M2butene (2)	85	15.0

P - PARAFFINS   (1) FEED FOR MTBE OR T-BUTANOL
O - OLEFINS   (2) FEED FOR TAME
A - AROMATICS
X - OXYGENATES

SOURCE FOR -OH RATES:

ROGER ATKINSON, CHEMICAL REV., 1985, 85, 69-201
"KINETICS AND MECHANISM OF GAS-PHASE REACTIONS OF HYDROXYL
RADICALS WITH ORGANIC COMPOUNDS UNDER ATMOSPHERIC CONDITIONS"

TABLE   4

"LOW EMISSION" GASOLINE

POSSIBLE SPECIFICATIONS

SUMMER RVP	7.8 PSI	MAX
AROMATICS	20 %	MAX
VOLATILE OLEFINS (C5 & LIGHTER)	1 %	MAX
WT. % OXYGEN	2 %	MIN

FIGURE 1
EFFECT OF AROMATICS ON TAILPIPE EMISSIONS

1986 HONDA & 1985 CAMARO

FIGURE 1
EFFECT OF AROMATICS ON TAILPIPE EMISSIONS

1986 HONDA & 1985 CAMARO

% CHANGE RELATIVE TO INDOLENE

VOL% AROMATICS IN FUEL

FIGURE 2
% REDUCTION IN TAILPIPE EMISSIONS
vs FUEL OXYGEN CONTENT
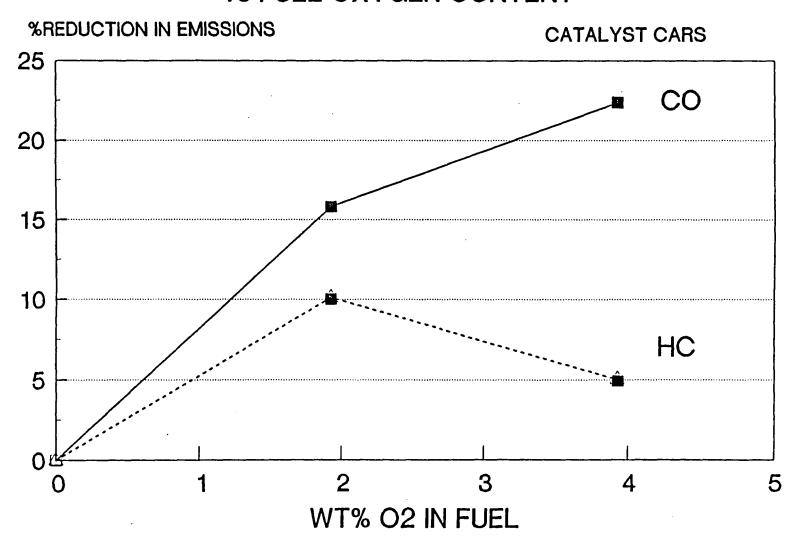
FIGURE 3A
% REDUCTION IN CO EMISSIONS
vs FUEL OXYGEN CONTENT

%REDUCTION IN CO EMISSIONS

CATALYST CARS

REFINERY BLENDED

SPLASH BLENDED

WT% O2 IN FUEL
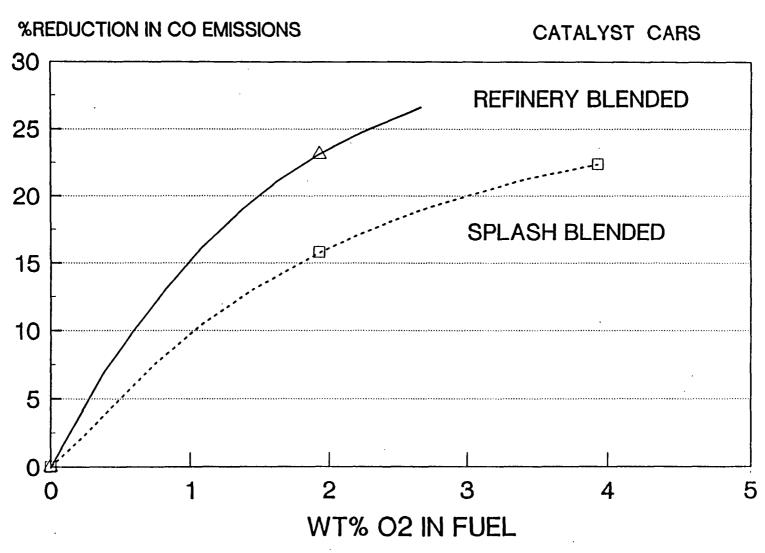
FIGURE 3B
% REDUCTION IN TAILPIPE HYDROCARBON
vs FUEL OXYGEN CONTENT

% REDUCTION IN UBHC EMISSIONS

CATALYST CARS

REFINERY BLENDED

SPLASH BLENDED

WT% O2 IN FUEL
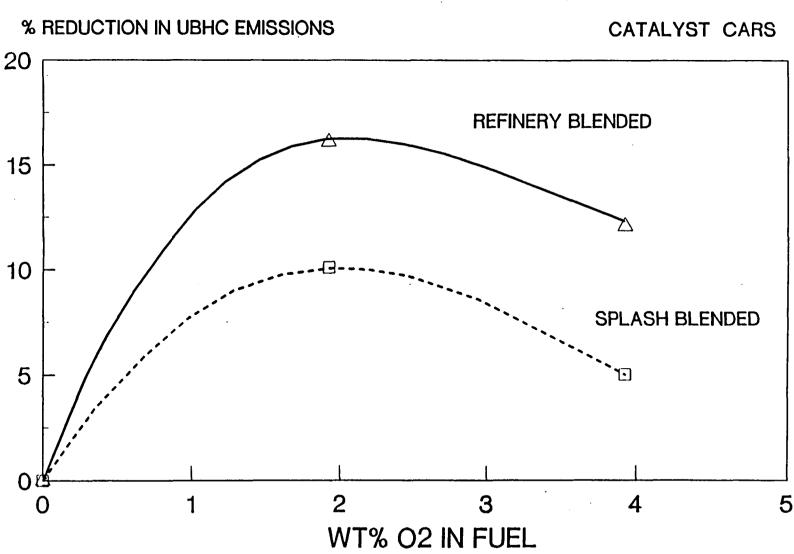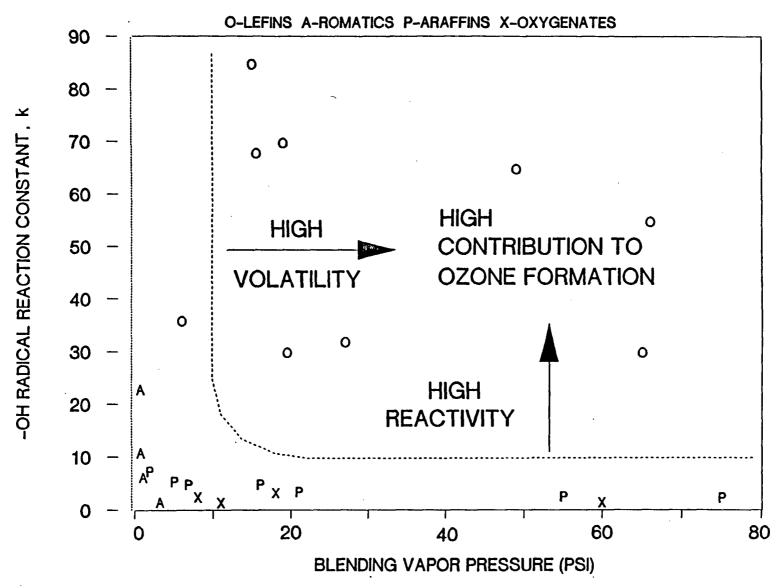
FIGURE 5
ATMOSPHERIC REACTIVITY
FOR VOLATILE GASOLINE HYDROCARBONS

O-LEFINS A-ROMATICS P-ARAFFINS X-OXYGENATES

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900153

Engine Bench Evaluation of Gasoline Composition Effect on Pollutants Conversion Rate by a Three-Way Catalyst

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ABSTRACT

The variety of the European refinery processes and the different strategies adopted by oil companies to meet gasoline octane ratings have given rise to a wide range of unleaded motor fuel characteristics. This study aims to examine the relations between gasoline quality, engine base emissions and catalyst performance.

Twelve fuels containing various amounts of aliphatic, olefinic, aromatic and oxygenated compounds were used in engine bench tests with a three-way catalyst. Rather large variations in the engine CO, HC and NO_x base emissions were observed with the nature of the fuel used. Conversion of these pollutants by the catalyst was then determined as a function of both temperature at stoichiometry and the A/F equivalence ratio at constant temperature. It was observed that nature of the fuel influences the catalyst light-off temperature and conversions at higher temperatures.

Data analysis shows that saturated hydrocarbons tend to minimize CO and NO_x emissions before the catalyst, whereas olefinics give the highest values. The reverse was observed for HC. A high aromatics content increases NO_x and HC emissions but is without any great influence on CO. Concerning catalyst activity, it was observed that the light-off temperature is decreased by the use of gasolines with a high olefin content, but is increased by aromatics. At higher temperatures the gasoline composition has very little or no effect on pollutant conversion at stoichiometry. Differences appear only for CO and HC on the rich side where saturated hydrocarbons give lower conversion rates.

INTRODUCTION

New legislative requirements in Europe concerning automotive emissions will necessitate the use of three-way catalysts on all new vehicles in the near future.

Since emission standards are based on vehicle emission characteristics in city traffic with a large contribution by idling and low-speed driving, the catalyst working temperature is rather low and the time required for its light-off is of great importance. A major portion of total emissions measured during a cold-start ECE city cycle usually occurs during the first or second minute of driving when the catalyst has not yet reached its minimum activation temperature (1)*.

It is thus of great importance to know if the gasoline formulation has any significant effect on the amount of each pollutant reaching the catalyst, on the catalyst light-off temperature, and on pollutant conversion.

Many studies concerning pollutant formation in engines have already shown that unburned hydrocarbons found in exhaust gas are either compounds originally present in the gasoline or molecules postformed from hydrocarbon fragments (2, 4). Very little is known from a quantitative point of view both for hydrocarbons and for CO and NO_x as a function of gasoline composition.

We describe here our first results obtained on a test bench with an engine equipped with a three-way catalyst and twelve fuels differing by their chemical composition and especially by their content of saturated, olefinic, aromatic and oxygenated hydrocarbons.

EXPERIMENTAL

THE DIFFERENT FUEL EXAMINED.

Twelve fuels were tested. Their main physico chemical characteristics are listed in Table 1. The first four fuels (ES1 to ES4) correspond to the specifications

---

* Numbers in parentheses designate references at end of paper.

2

300:

Table 1 - Characteristics of tested gasolines

CHARACTERISTICS	ES1	FS?	BF?	CO?	MTBE20	ETBE10	E10	FCC	REFORM	SPL	ISOC8	ALK
Density @ 15°C (kg/l)	0.7519	0.7594	0.7467	0.7448	0.7508	0.7518	0.7541	0.6995	0.7758	0.7821	0.6960	0.6975
RVP (hPa)	715	457	473	566	654	626	718	749	591	641	•	456
Distillation												
IBP (°C)	27.0	35.0	35.0	35.0	33.6	31.0	31.5	31.0	28.9	32.0	94.2	33.3
% vol evaporated @ 70°C	24.0	16.4	19.1	00.0	32.4	22.1	38.5	83.1	24.6	23.1		8.8
% vol evaporated @ 100°C	45.2	39.2	38.1	50.0	51.8	49.5	53.6	80.7	42.3	42.3		30.0
EBP (°C)	190.0	205.0	195.0	196.0	188.0	189.5	188.5	169.5	190.0	207.5	99.5	117.0
Sulphur (%w)	0.008	0.015	0.009	0.011	0.004	0.001	0.004	0.020	0.001	0.004	0.000	0.001
FIA Analysis (%vol)												
Saturates	56.3	55.3	49.8	69.4	51.0	49.3	54.0	41.8	47.6	29.5	100.0	>98.0
Olefins	8.2	4.5	18.8	6.5	8.0	7.7	7.4	49.1	<1.0	12.0	0.0	<1.0
Aromatics	35.5	40.2	31.4	24.0	41.0	43.0	38.6	9.1	51.4	58.5	0.0	<1.0
C (%w)	86.80	87.15	86.80	86.50	82.70	85.35	83.00	83.40	84.70	00.00	84.10	81.33
H (%w)	12.90	12.85	13.10	13.10	13.10	13.00	13.00	13.70	11.30	11.90	15.89	13.73
O (%w)	0.00	0.00	0.00	0.00	3.60	1.65	3.80	0.00	0.00	1.65	0.00	0.00
Gross heating value (kJ/kg)	45200	45555	45748	45785	43328	45139	44010	46161	44092	43920	47806	47935
RON	95.5	95.6	98.4	96.5	99.6	98.0	98.7	93.3	99.2	101.5	100.0	95.2
MON	85.9	86.0	85.4	86.1	88.3	87.1	87.5	80.6	88.7	88.7	100.0	92.8

for standard European unleaded gasoline (4). They differ by their content of saturates, olefins, and aromatics according to the different refining schemes chosen to meet the target of 95 RON - 85 RON. ES1 was taken as a reference fuel during all the tests.

The influence of oxygenates was examined by adding three different oxygenated compounds to reference fuel ES1. The first one, MTBE 20, contained 20% volume of methyltertiobutylether, ETBE 10 contained 10% ethyltertiobutylether, and E10 10% ethanol.

To increase the difference in the chemical composition among fuels, products having more typical characteristics were also selected. This is the case, for instance, for some refining base stocks, e.g. FCC is a light gasoline from catalytic cracking with a very high olefin content (49.1%) and consequently high sensitivity (difference between RON and MON). A high-severity reformate (REFORM) and a high-grade unleaded gasoline recently marketed in France (SPL) were selected to test the effect of aromatics. These two fuels have an aromatic content higher than 50%, high density and high octane numbers. The influence of paraffinic components was studied first using pure isooctane and then with an alkylate (ALK), which contains more than 98% isoparaffins but has physical characteristics (except for density) close to those of commercial gasoline.

THE ENGINE BENCH SET UP used for the tests has already been described (6). It is composed of a 2.2 liter engine equipped with a port-injected EFI system. As implemented the EFI system enabled the engine's A/F ratio to be controlled by using feedback from an EGO sensor or to be monitored externally in open loop. No A/F perturbation was surimposed to the low amplitude oscillations (± 0.0025 Ø) usually observed.

Exhaust gas temperature was monitored by cooling (fan) or heating (electric heater) the exhaust pipe ahead of the catalytic muffler. All tests were performed with a constant exhaust gas flow of 46.6 m³. h⁻¹ NTP, with the engine running at 2500 rpm with a load of 13.5 hp.

Steady-state emission concentrations were measured before and after the catalyst using conventional exhaust gas analyzers. The A/F equivalence ratio was determined both chemically from these measurements (on-line minicomputer used for calculations) and by the mean of an A/F ratio analyzer (Lamdascan III from Cussons).

The CATALYST used in these studies was of the three-way type. It was prepared on a Cordierite monolith substrate having a nominal cell density of 62 cells per cm² (400 cells per sq. inch) with 160 μm wall thickness. Its cross-section was circular with a diameter of 11.8 cm (4.66 in), a height of 7.6 cm (3 in) and a volume of 840 cm³ (51.2 in³).

An alumina based wash-coat containing, among other additives, 4.5% cerium oxide was applied on this monolith (100 g/l). The noble metal content was 1.06 g/L (30 g/CF) with a platinum/rhodium ratio of 5/1.

The catalyst age varied between 25 hrs and 120 hrs from the beginning to the end of the series of tests made.

Both temperature traverse (% conversion vs temperature) and A/F equivalence ratio traverse (% conversion vs A/F equivalence ratio) catalyst performance data were obtained by changing the inlet gas temperature, or equivalence ratio, step by step (with around 10 to 20 min stabilization between each point), with all other parameters remaining constant.

The catalyst was preconditioned, before testing each new fuel, by running the engine with the same reference fuel (ES1) in closed-loop conditions with an inlet gas temperature of 500°C.

The experimental results given below will concern the catalyst light-off temperature (i.e. the temperature necessary for 50% CO, HC or NO_X conversion), the mean CO, HC and NO_X conversions C_T at stoichiometry between 300°C and 550°C, and the mean CO, HC and NO_X conversions C_R at 450°C with A/F equivalence ratios between 0.9 and 1.04. These mean conversions were calculated as follows:

3

$$C_T = \int_{T_1}^{T_2} C. \, d\, T/T$$
with $T_1 = 300°C$ and $T_2 = 550°C$

$$C_R = \int_{R_1}^{R_2} C. \, d\, R/R$$
with $R_1 = 0.96$ and $R_2 = 1.04$

The repeatability of the measurements was checked using the same fuel (ES1) at the beginning and end of the series of tests. Table 2 shows that only very minor differences were observed.

Table 2 - Repeatability of measurements: results obtained with reference fuel ES1 at the beginning and end of the series of tests

	1st test			2nd test		
	CO	HC	NO_x	CO	HC	NO_x
Inlet ppm	8762	8993	2656	8765	8989	2665
T_{50} (°C)	316	324	317	315	323	315
C_T (°C)	93.3	87.4	69.8	93.6	87.1	67.4
C_R (%)	79.6	80	59.2	78.5	79.7	59.9

RESULTS AND DISCUSSION

ENGINE BASE EMISSIONS - The level of CO. HC. NO_x and O_2 concentrations measured before the catalyst with the different fuels tested, with the engine running under closed-loop A/F control at stoichiometry, are given in Figure 1. Rather large variations are observed between the minimum and maximum values: 83% for CO, 33% for HC, 58.4% for NO_x and 38.4% for O_2.

In accordance with the fact that the engine runs at a constant A/F equivalence ratio, we found that when CO emissions increase there is a simultaneous increase in O_2 and NO_x emissions, as shown in Figure 2. We also generally found that, when CO emissions increase, HC emissions decrease (the two oxygen-containing fuels, E10 and ETBE 10, do not, however, follow this correlation).

We generally assume that the hydrocarbons that remain after the primary engine combustion process are partly oxidized further during the expansion and exhaust process (7,8). Since oxygen is thus at a low concentration, HC oxidation results in an increase in the CO level. Since the HC burnup rate is influenced by the reactivity of each hydrocarbon species, it is thus normal to find a higher amount of unburnt HC (and a lower amount of CO) when the fuel is composed of saturated hydrocarbons (ISOC 8 or ALK) with low reactivity. On the contrary, olefinic hydrocarbons can react more easily; and we actually observed a low HC emission level and a high CO emission level with the FCC fuel.

NO_x emissions are strongly dependent on flame temperature. Saturates and oxygenates generally lead to low flame temperature and thus low NO_x emissions. On the contrary, aromatic hydrocarbons produce a higher flame temperature, which may be due to a higher combustion rate. These tendencies are clearly observed here.

From the point of view of "cleanliness" it is difficult to say which of these fuels is the best because, whereas the lowest emissions of HC are obtained with
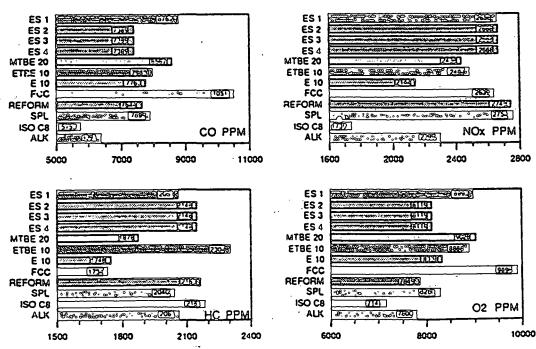

Figure 1 - Engine CO. HC. NO_x and O_2 base emissions (ppm) before the catalyst with the different fuels tested, under closed-loop A/F control at stoichiometry, 2500 rpm and 13.5 hp.
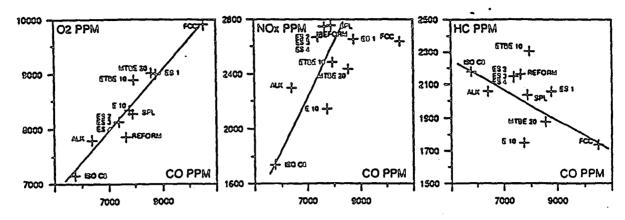
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Figure 2 - Correlation between engine CO, HC, NOx and O2 base emissions.

the FCC fuel, this fuel produces maximum emissions of CO and NOx. The contrary is obtained when isooctane is used as a fuel.

POLLUTANT CONVERSIONS by the three-way catalyst were determined with each of the twelve fuels, first as a function of exhaust gas temperature under A/F control at stoichiometry, and then as a function of the A/F equivalence ratio with a constant exhaust gas temperature of 450°C. The exhaust gas flow was constant in each case, and the gas hourly space velocity through the catalyst was 55,000 h^{-1}.

Typical conversion curves obtained with the reference fuel used (ES1) are given in Figures 3 and 4.

The values for the light-off temperature, T_{50}, the mean conversions, C_T, at stoichiometry between 300 and 550°C, and the mean conversion, C_R, at 450°C with A/F equivalence ratios between 0.96 and 1.04, obtained with the twelve fuels tested are given in Table 3.

Concerning exhaust gas temperature the main effect observed for CO and HC conversions concerned the light-off temperature. The maximum difference was in the range of 20-25°C (Figure 5). The lowest light-off temperature was obtained with the FCC fuel having a high olefin content, and the highest with the two fuels (Reformat and SPL) having a high aromatics content.

This is in accordance with measurements made concerning the ability of pure hydrocarbons to be converted on three-way catalysts. Laboratory experiments have actually shown that the oxidation of olefinic hydrocarbons is converted at lower temperatures than aromatics (9). Oxygenated additives do not seem to significantly modify the catalyst light-off temperature.

For NOx conversion, differences were observed both for light-off and for conversions at high temperatures. The highest conversion rate was observed in this latter case for isooctane and then for Reformat (high aro-

Table 3 - Temperature for 50% CO, HC or NOx conversion at stoichiometry (T_{50}), mean CO, HC and NOx conversion between 300 and 500°C at stoichiometry (C_T), and mean CO, HC and NOx conversion at 450°C with an A/F equivalence ratio between 0.96 and 1.04 (C_R); Pt-Rh three-way catalyst, GHSV = 50,000 h^{-1}.

Fuel	T_{50} (°C)			C_T (%)			C_R (%)		
	CO	HC	NOx	CO	HC	NOx	CO	HC	NOx
ES1	316	324	317	93.3	87.4	69.8	79.8	80	59.2
ES2	315	323	316	93.7	88.3	74.2	78.7	80.5	58.5
ES3	324	329	323	90.2	86.1	69.7	77.3	80	58.4
MTBE 20	320	326	320	92.4	86.3	68.1	78.7	80.7	59
ETBE 20	324	332	324	90.4	85	67.8	79	81.1	58.6
E10	324	332	322	90.4	85	71.2	78.5	81.2	59
FCC	308	314	308	96.1	90.5	71.2	77.4	82.5	59.3
REFORM	330	336	330	88.2	82.3	72	79.1	81.2	57.6
SPL	332	336	331	87.9	82.3	68.2	79.1	81.8	59.2
ISO C8	324	330	324	90	84.1	78.8	71.4	72.7	59.6
ALK	324	328	324	89.9	84.8	71.2	75.3	76.3	58.3
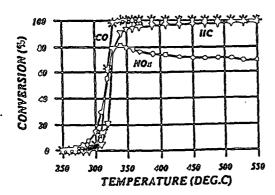
Figure 3 - CO, HC and NO_x stoichiometric light-off conversions with ES1 fuel:

Figure 4 - CO, HC and NO_x conversions versus A/F equivalence ratio with ES1 fuel at 450°C.

matics content). It is not very clear, however, if these results for NO_x conversion are meaningful due to some variability in NO conversion in this range of the conversion curves.

Concerning the effect of the A/F equivalence ratio, differences on CO and HC conversions are observed only on the rich side, above $\Theta= 1.00$. Figure 6 shows the effect of a fuel change on CO and HC conversions at $\Theta= 1.02$ and 450°C. Conversions are very similar, except for two saturated fuels (isooctane and alkylate) which showed lower conversion rates: respectively 55 and 50% conversion versus a mean conversion of 65 to 70% for CO with the other fuels and 45 and 35% versus 55 to 60% for HC with the other fuels.

This is probably related to the lesser ability of saturated hydrocarbons to be converted by a steam reforming reaction when oxygen is deficient in the exhaust gas.

NO_x conversions are nearly the same with the different fuels at equivalence ratios above 1.00. On the lean side some small differences can be seen but are probably not meaningful.

SUMMARY AND CONCLUSIONS

This report gives the first results obtained in research undertaken to determine gasoline composition effect on CO, HC and NO_x base emissions by engines working under A/F closed-loop control at stoichiometry and on the pollutant conversion efficiency of three-way catalysts.

Twelve fuels containing various proportions of saturated, olefinic, aromatic or oxygenated hydrocarbons were tested.

1. Concerning the base emissions by an engine working at constant load and speed, the main conclusions were:
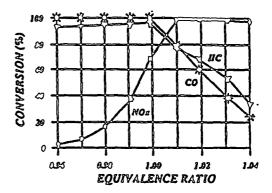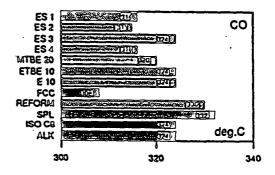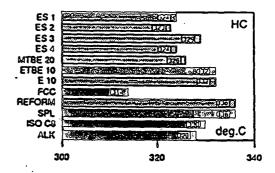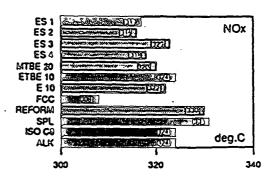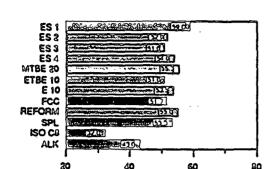

Figure 5 - Temperature necessary for 50% CO, HC or NO_x conversion under closed-loop control at stoichiometry, with the different fuels tested.
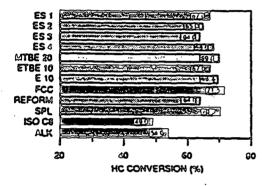
6

Figure 6 - CO and HC conversions at an A/F equivalence ratio of 1.02 (rich) at 450° with the different fuels tested.

- o Saturated hydrocarbons, such as isooctane or products obtained in refineries by alkylation, minimize CO formation, whereas olefinic give the highest levels,

- o A high aromatics content increases NO and HC levels but is without any great influence on CO.

2. Concerning pollutant conversion by a three-way catalyst it was observed that:

- o The catalyst light-off temperature is at a minimum for CO, HC and NO_x when a gasoline with a high olefin content is used, but it is increased by the use of a gasoline with a high aromatics content.

- o At higher temperatures and at stoichiometry, the gasoline composition has no effect on CO and HC conversions (some variations, to be confirmed, have been observed for NO_x).

- o When the A/F equivalence ratio departs from 1.00 the gasoline composition modifies CO and HC conversions on the rich side, but it has no effect on the lean side.

Gasoline chemical formulations thus have a non-negligible influence on engine base emissions and on catalyst efficiency. The differences are sometimes relatively

great. It must be pointed out however that all these experiments were performed with an engine and a catalyst working in stabilized conditions. The unburned hydrocarbons present in the exhaust gases were mainly hydrocarbons transformed by pyrolysis and partial oxidation. For a vehicle, due to poor combustion at start and during transient conditions, since the gasoline components are present in a larger amount, an even more pronounced effect should be observed.

AKNOWLEDGMENTS

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ATTACHMENT 9-4

NATIONAL PETROLEUM REFINERS ASSOCIATION

AM-90-31

MAINTAINING PRODUCT QUALITY
IN A REGULATORY ENVIRONMENT

by

George H. Unzelman
President

Hy Ox Inc.
Fallbrook, California

Presented at the

1990 NPRA
ANNUAL MEETING
March 25-27, 1990
Convention Center
San Antonio, Texas

MAINTAINING PRODUCT QUALITY IN A REGULATORY ENVIRONMENT

by George H. Unzelman

SUMMATION

Maintaining transportation fuel quality in the regulatory environment that can now be projected for the 1990 decade will become a balancing act between regulating agencies and the petroleum refining industry. Regulations modifying gasoline and diesel fuel composition will be promulgated to improve air quality and reduce human exposure to critical hydrocarbons. Given enough time to generate capital and install processing the market can be kept in reasonable balance.

Agency targets include additional gasoline volatility control, an upper limit on benzene in gasoline and restrictions on undesirable hydrocarbons in both gasoline and diesel fuel. To some degree the processing moves necessary to control gasoline composition also will modify diesel fuel composition.

Regulatory action may require application of alternative fuels in critical air pollution areas such as Los Angeles. For example, Colorado has pointed the way by requiring oxygenates in gasoline in Denver and other Front Range cities during winter months to control carbon monoxide emissions.

The petroleum industry has recognized the need to reformulate gasoline, not only to meet forthcoming federal and state regulations, but to protect the crude-oil-derived transportation fuel market. The first stage of an extensive joint oil/auto industry research and testing program is underway to target the best fuel composition to reduce emissions, especially those contributing to ground-level ozone formation. Early indications of possible specifications for reformulated gasoline are based on current "emission control" gasolines and EPA studies for future rulemaking.

Summer Rvp of gasoline may be 1 to 2 psi lower, aromatics could be limited at some point between 25 and 30 volume percent with additional control on benzene at the 0.5 to 1.0 volume percent level. Olefin content may be restricted by limiting the bromine number of gasoline. However, setting limits on total volume percent aromatics and olefins may be flawed because it does not necessarily eliminate critical reactive hydrocarbons.

The most difficult petroleum refining maneuver to meet reformulated gasoline targets, commensurate with maintenance of quality, will be aromatics reduction. Ethers are the only refinery components that have the potential to replace aromatics. However, with further Rvp restrictions the manufacture and blending of ethers will tend to alleviate the gasoline volatility problem. Adjustments to the U.S. gasoline pool to meet reformulated fuel targets and maintain reasonable grade quality will require most of the 1990 decade.

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CONCLUSIONS

◦Current octane quality of the U.S. gasoline pool (88.4 ON) seems adequate for gasoline-grade distribution of the 1990 decade. However this quality level may be difficult to maintain with fuel changes needed to control air quality.

◦Atmospheric reactivity of gasoline components can be estimated by the gas-phase reaction with the hydroxyl radical. Of the hydrocarbon groups, least reactive are paraffins followed by aromatics and olefins. Alcohols and ethers have low atmospheric reactivity.

◦Most troublesome hydrocarbons are: (1) benzene because it is a known carcinogen (2) xylenes and heavier aromatics because of high atmospheric reactivity (3) light olefins because of extremely high reactivity and high vapor pressure. All of these hydrocarbons are key contributors to octane in the current gasoline pool.

◦Ethers can be substituted for high-octane hydrocarbons that may be restricted from U.S. gasoline. Aromatic control must come from less severe naphtha reforming and lower cat cracking conversion. Critical light C_5 olefins can be removed by etherification eg conversion to tertiary amyl methyl ether. Side benefits of aromatic and olefin reduction can be greater gasoline yield and reduced volatility.

◦The manganese antiknock (MMT), if approved for unleaded gasoline, could replace significant octane lost from removing high-octane hydrocarbons, primarily aromatics.

◦Study of the U.S. gasoline pool composition implies that processing changes are feasible to lower average-summer vapor pressure to 9 psi and to reduce aromatics from 32 to 30 volume percent (close to 28 volume percent with MMT).

◦It is unlikely that U.S. gasoline pool aromatics can be reduced to 25 volume percent in the petroleum refining framework of the 1990 decade without a compromise of marketed-octane quality.

◦Special gasolines with 20-25 volume percent aromatics, mandated oxygenates etc. are feasible for critical environmental areas. Such gasolines are possible at the expense of transferring less desireable components to other grades or other market areas.

◦Small refineries and independent refiners with limited processing flexibility and/or capital will feel the greatest pressure from regulations altering fuel composition. The 1990 era will be analogous to the critical lead phasedown years. Further industry consolidation and more foreign ownership can be expected.

THE GASOLINE POOL AND GRADE QUALITY

Background

The lead phasedown had a major impact on the composition of the U.S. gasoline pool. Overall volatility increased, the concentration of aromatics and isoparaffins increased. Low-octane normal paraffins were minimized. MTBE (methyl tertiary butyl ether) was introduced as the only non-hydrocarbon, refinery-pool component to increase octane quality. By the end of 1987 the major impact of lead removal on pool-composition changes was essentially complete. Allowable lead content in the leaded pool was reduced to 0.1 gms. of lead per gallon and the leaded grade was destined to decline at the rate of about 5 to 6 percentage points per year in concert with the attrition of lead tolerant vehicles on the road.

However, the American public's appetite for sizeable cars with adequate power output worked in tandem with the lead phasedown to continue the changes in gasoline-pool hydrocarbon composition. The oil industry seized the opportunity to aggressively market more profitable unleaded premium. Competition for premium volume resulted in higher-octane, premium-fuel quality at the pump, particularly at Eastern U.S. outlets. The increasing demand for high-octane premium fuel pushed gasoline-pool aromatics upward and placed more emphasis on etherification and isomerization processing in petroleum refining.

U.S. Gasoline Pool Composition

Table I shows the approximate composition and octane range of refinery components that made up the average 1988 gasoline pool (1). In retrospect the stream composition was somewhat aggressive with the volume percents for isomerate and MTBE for 1988; also the light straightrun figure was low. Therefore the volume percents and octane ranges are a reasonable representation for 1989. An aromatics range and average total for pool aromatics has been added to the earlier documentation (1) which keys to industry data. In order to reach the clear pool octane of 88.4, aromatics have increased to slightly over 32 volume percent. In 1980 the U.S. unleaded gasoline pool was about 83 octane and the aromatic concentration was 10 numbers lower at 22 volume percent. Current aromatic content of the gasoline pool has been established from Motor Vehicle Manufacturers Association data (2) and by extrapolation of earlier Ethyl Corporation information (3). The range of aromatics in stream compositions is taken from typical industry samples and fitted to the gasoline-pool total of 32.1 volume percent.

U.S. Gasoline Grade Mix

Table II is an estimate of the U.S. gasoline grade mix for 1988 (1). In the summer of 1989 the higher price at the pump for premium gasoline dampened the market and some volume shifted back to the unleaded regular grade. Table III is a current estimate of the U.S. gasoline-grade mix for 1989 which reflects the shift away from premium and declining volume of the leaded grade. Unleaded premium has lost about 3 percentage points but has increased to an average of 92.5 in octane quality. Leaded regular has dropped to 10 volume percent and unleaded regular now has about 60 percent of the market. "Average clear octane" at 88.5 of the grade mix has slipped fractionally but has been relatively stable for the past 18 months. In fact, this is the first period of pool-octane stability since the lead phasedown in the mid-1970's.

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Temporary Gasoline Pool Composition Stability

To some extent the stability of hydrocarbon composition of the gasoline pool has paralleled stationary-clear pool octane. Aromatic content has leveled and possibly even declined fractionally. There has been a modest drain on pool octane from restrictions on summer Reid vapor pressure (essentially less n-butane) and the declining amount of lead antiknocks used in gasoline. The balancing octane factors are from more MTBE and the gradual and continuing exchange of isoparaffins for normal paraffins, primarily from isomerization.

Octane Quality Issues of the 1990's

The so-called period of hydrocarbon-composition stability for the gasoline pool may continue for a limited period, but it is destined to end with the fuel regulations that are currently projected to control air quality. New rules governing fuel composition will impact on hydrocarbons that are high in octane quality, specifically aromatics, light olefins, and n-butane. As these rules restrict key-octane contributors to gasoline, there is the question of maintaining product quality at the gasoline pump. The situation actually boils down to retaining an octane balance between Table II (grade mix) and Table I (pool composition). It can be accomplished with the promulgation of reasonable fuel-composition standards and achievable industry timetables to install new processing.

Table III with an average clear octane quality of 88.5 should provide a satisfactory average octane quality for cars of the 1990 decade. Assuming leaded regular disappears from the market place and midgrade is combined with premium, the grade ratio would approximate a 30/70, premium/regular fuel ratio. This is not too far afield from the traditional premium/regular ratio of 40/60 of the early 1970's. The basic industry challenge will be to shift the composition of the gasoline pool of Table I to satisfy both regulations and grade mix requirements.

CRITICAL HYDROCARBONS SUBJECT TO REGULATION

General Background, Hydrocarbons

The oil industry has known the octane values for most hydrocarbons in the gasoline boiling range since early in the century. Blending values changed as gasoline composition changed but the quality of individual hydrocarbons held within a fairly narrow range. Except for n-butane, the normal paraffins are low in octane. Comparable isomers are much higher octane. In unleaded gasoline, aromatics, olefins, and isoparaffins provide the basic octane structure generally in that order of magnitude. Again, except for normal butane, the normal paraffins are limited by low-octane quality.

Today there is a good deal of background about which classes of hydrocarbons are "good" and "not so good" with respect to environmental factors. And the scientific community is continuing to learn more about individual hydrocarbons as they relate to public health.

For example, although gasoline generally contains only a small amount of benzene (1-5 volume percent), the impact of this particular high-octane aromatic on human health is under study because it is a known carcinogen. In fact, aromatic hydrocarbons in general have attracted the attention of environmental groups because the concentration in gasoline has steadily increased in recent years.

Aromatics are not only high in octane quality as shown in Table IV, but they have low vapor pressures and consequently the capacity to modify the volatility impact of light hydrocarbons in gasoline blending operations (4). N-butane, the only normal paraffin with a (R+M)/2 blending octane

above 90, has the disadvantage of having a blending Reid vapor pressure (Rvp) of about 60 psi. This is a distinct disadvantage with the current summer EPA limits on gasoline Rvp specifications to help control ground-level ozone formation. Also, the schedule for the early 1990's calls for further restrictions on gasoline Rvp.

Atmospheric Reactivity, Hydrocarbons

While benzene is undesirable from the standpoint of human health and n-butane has limitations because of high-blending-vapor pressure, both compounds have low reactivity values based on the gas-phase reaction with the hydroxyl radical at atmospheric conditions. The so-called OH reaction rate gives an indication of photochemical reactivity with respect to ground-level ozone formation (5). Table V lists these values along with blending Reid vapor pressure for representatives of three hydrocarbon classes; paraffins, aromatics, and olefins. Values also are shown for five oxygenates.

Both n-paraffins and isoparaffins have low atmospheric reactivity. The exchange of n-paraffins for higher-octane isoparaffins in the gasoline pool, which will continue as more isomerization units are installed, will have little effect on reactivity. On the other hand isomers are more volatile and their continued influx to the pool will require removal of additional n-butane.

Atmospheric Reactivity, Aromatics

In general, the heavy aromatics exhibit greater reactivity than benzene and toluene. (See Table IV, xylenes and heavier) Because of high boiling points, there is less concern about reactivity with respect to evaporative emissions. However as butanes and other light hydrocarbons escape as vapor, some of the heavier hydrocarbons are carried along. At the same time, the heavy aromatics can enter the atmosphere from spillage and from under the hood of vehicles during "soak periods" especially during warm weather. Also, they are comparatively more difficult to combust and have greater tendency to appear as part of tailpipe hydrocarbon emissions. The heavy aromatics also contribute to tailpipe benzene from decomposition during engine combustion.

The EPA as well as state agencies have studied benzene restrictions in gasoline and may additionally place some limit on overall aromatics. The most favorable gasoline aromatic is toluene because it has low atmospheric reactivity, high octane quality, less toxicity than benzene, and tends to combust more completely in the engine than the heavier aromatics.

Atmospheric Reactivity, Olefins

As a group, the olefins are high in photochemical reactivity. Most of the olefins in today's gasoline come from fluid cat cracked gasoline and represent an important factor in "front-end" octane. In other words, the light olefins, along with n-butane, contribute octane quality in the low-boiling segment of gasoline as defined by the ASTM distillation curve. Several of the light olefins have blending octanes that exceed 100 at low concentrations.

Generally C_4 olefins are routed at the refinery to alkylation, petrochemical operations, and MTBE processing. Very little is blended directly to gasoline. Listed in Table V are two very photochemically reactive C_5 olefins, 2-methyl 2 butene and 2-methyl 1 butene, that appear in the front end of fluid cat cracked gasoline. Both have relatively high vapor pressures (15 and 19 psi respectively) and are subject to being significant contributors to evaporative emissions. While the

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heavier olefins in gasoline have equal or greater photochemical reactivity, there is less tendency to escape to the atmosphere.

Suggestions to control total olefins in gasoline via a limit on bromine number may be flawed because it would not necessarily restrict these most critical hydrocarbons from gasoline. The problem was summarized succinctly by Dr. Edgar R. Stevens, professor of Environmental Sciences and Chemistry at the University of California at Riverside. In his letter to the Advisory Council of the South Coast Air Quality Management District in 1987, Dr. Stevens is quoted as follows:

"The most reactive component of gasoline currently marketed in Southern California is the olefin fraction. This has been recognized for many years. Thirty years ago, it was suggested that elimination of olefins from gasoline might eliminate smog, without the necessity of control devices for every car. When research showed that this "quick fix" would not work, the idea was abandoned although a limit of 15% was placed on the olefin content of gasoline. Now that so many strategies of marginal effect are being seriously considered perhaps it is time to reconsider the olefin limitation as a contributor to smog control."

Later in the same correspondence Dr. Stephens made the suggestion that critical olefins be removed by etherification.

OXYGENATE SUBSTITUTION FOR CRITICAL HIGH-OCTANE HYDROCARBONS

Atmospheric Reactivity — Oxygenates

The last category on Table V lists atmospheric or photochemical reactivity figures for methanol, ethanol, MTBE, ETBE (ethyl tertiary butyl ether), and TAME (tertiary amyl methyl ether). All of the values are low and are comparable to paraffin-hydrocarbons.

Alcohols as Gasoline Blending Agents

Table VI lists blending octane, blending Rvp, and the boiling point for the five oxygenates that have potential as blending agents in gasoline. Methanol must be used with cosolvents if blended to gasoline. For a time in the 1980's methanol was marketed in various combinations with TBA (tertiary butyl alcohol) by ARCO Chemical Co. under the trade name Oxinol. Ethanol is currently blended downstream of the refinery to the extent of about 60,000 B/D and constitutes 0.8 volume percent of U.S. gasoline. "Downstream blending" accounts for the octane differential (average) of 0.1 numbers between Table III (U.S. Gasoline Grade Mix, 88.5) and Table I (Average U.S. Gasoline Pool Composition, 88.4). Ethanol as 10 percent of gasohol contributes significantly to the difference.

The experience of the last decade indicates the alcohols have little attraction for refinery blending. They are not water tolerant and they exhibit high blending vapor pressures with hydrocarbons. For example methanol has about the same blending vapor pressure in gasoline as n-butane while ethanol blends in the Rvp range of n-pentane and isopentane. Their low photochemical reactivity values tend to be negated by azeotropic characteristics which greatly increase blending vapor pressure in combination with hydrocarbons at low concentrations. This represents a serious economic penalty for refiners who must blend to ASTM specifications. On the other hand pure methanol has a Rvp of only 4.6 psi. Also mixtures of methanol and gasoline such as M-85 (85% methanol) are relatively low in vapor pressure. The President's Clean Air Act proposal, as well as many agencies representing critical air pollution areas, strongly support methanol fuels.

MTBE — Methyl Tertiary Butyl Ether

MTBE has a blending octane ranging between 106 and 110, Rvp between 8 and 10, and photochemical reactivity of 2.6, close to that of n-butane. It is manufactured at the refinery, blended and transported in the same wet systems that handle hydrocarbons. Growth for this methyl ether has been rapid -- from essentially zero in 1980 to 100,000 B/D in today's gasoline pool.

On the other hand this growth has been logical and natural for the petroleum refining industry. A high percentage of early construction took place in the Southwest where both isobutylene from steam cracking and methanol feedstocks were economically available. Because of the convenient isobutylene, the capital cost for MTBE processing facilities was moderate. With the pressure of the lead phasedown, an MTBE plant could not only generate high octane blend stock but unload alkylation capacity to process alternative-olefin feedstock. It allowed a timely addition to pool-octane quality from two refinery units.

More recently refiners have based ether producing facilities on the isobutylene from fluid cat cracking operations. Because less isobutylene is available at lower stream concentration, these units are smaller and have higher per barrel cost. As the environmental demand for refinery-compatible oxygenates grows, it will be necessary to manufacture more isobutylene from n-butane by isomerization and dehydrogenation, a more capital intensive approach. For example, Phillips has recently announced engineering for such a plant (7500 B/D) at Borger, Texas. An alternative for small refiners will be to purchase merchant MTBE which should be available from U.S. producers as well as from world-scale-methanol plants producing coproduct ether.

MTBE as a Substitute for Aromatics

While MTBE will continue to increase in volume in the gasoline pool, it is not a "one on one" replacement for aromatics. In general the blending octane quality is higher than most of the pure aromatics listed in Table IV but the blending vapor pressure of the aromatics is much lower. Capacity to absorb n-butane is important to gasoline blending economics and will become increasingly so with more stringent environmental restrictions on Rvp. For example, the blending Rvp for toluene is about 0.5 psi versus MTBE in the 8 to 10 range (6). Boiling point difference is another factor because it impacts the ASTM distillation curve. Pure MTBE boils at 131°F versus a 250°F plus average for aromatics.

Naphtha Reforming Adjustment to Reduce Aromatics

While it is interesting to compare the substitution of MTBE for aromatics on a direct basis, the processing adjustment at the refinery would be made by modifying naphtha reformer operations as well as other units. However the reformer can be used as the example. Table VII exhibits yield inspection data for two operating conditions (7). Volume percent aromatics of the pentanes plus (gasoline) fraction and (R+M)/2 octane has been estimated from industry data. As reformer severity (measured by Research octane) is increased from 90 to 95, aromatics of the gasoline fraction (pentanes plus) increases about 8 volume percent. (R+M)/2 octane increases 4 numbers and gasoline yield falls 3.7 volume percent.

Conversely the addition of 5 volume percent MTBE to pool gasoline would allow reformer severity to back off about one (R+M)/2 octane, thus reducing reformate aromatics by 2 volume percent. Gasoline yield would increase about 0.9 volume percent. Further the Rvp of the gasoline yield would drop slightly, about 0.1 psi. Overall the gasoline pool would directionally increase in API

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gravity as a result of the introduction of MTBE and the elimination of some aromatics. The trade off would tend to move the entire gasoline pool in the direction of cleaner burning composition.

ETBE — Ethyl Tertiary Butyl Ether

Obviously MTBE is not the only ether that has the potential to replace aromatics from gasoline. ETBE has a slightly higher octane quality than the methyl ether and lower blending vapor pressure, 3 - 5 psi depending on the hydrocarbon composition of the gasoline. Because mixed aromatics have a blending vapor pressure of less than 1 psi, the ethyl ether would be more attractive for Rvp control. Much depends on feedstock economics and whether ethanol feedstock will be subsidized. At this writing the U.S. Internal Revenue Service is receiving comments following a 1/4/90 hearing on the proposal to make ETBE eligible for the 60¢/gallon tax credit for the percent of ethanol "contained". A favorable decision would shift some current MTBE units to ethanol or mixed methanol/ethanol feed. Future new, units could be designed for ETBE rather than MTBE, particularly in the farm states that might follow the federal move with state subsidies. ETBE has strong support from the Executive Branch. President Bush in remarks, January 8, 1990 to the American Farm Bureau in Orlando, Florida said:

> "Just a few months ago, we proposed the expansion of the producer tax credit for alternative fuels to include ETBE. This will mean more markets for growers and cleaner air for all Americans."

TAME — Tertiary Amyl Methyl Ether

The most reactive hydrocarbons shown in Table V are the C_5 olefins, 2-methyl 2 butene and 2-methyl 1 butene. Both are components of fluid cat cracked gasoline and have blending octane quality in the 100 range and vapor pressure of 15 and 20 psi. They can be converted to TAME via the reactions with methanol. The conversion results in a methyl ether with octane quality above 100 and blending vapor pressure in the 1 - 2 psi range.

Current plants in England and France actually manufacture "TAME gasoline" rather than a relatively pure ether stream. The front end of cat cracked gasoline is used as the olefin feed stream and the critical C_5 olefins are converted to ether. There is little doubt that the C_5 olefins, some of the most reactive with respect to ozone formation, will be under severe pressure in the 1990's as the study of fuel reformulation progresses. In 1989 ARCO Chemical authors (8) summarized the advantages of TAME to the environment:

> "Of all the ethers, TAME can probably provide the most environmental benefit. It reduces tailpipe emissions and converts some very volatile and highly reactive C_5 olefins in the gasoline pool into a very low Rvp and clean burning ether. This Rvp reduction will also provide the refiner with added flexibility in meeting the future Rvp control regulations. Unlike the Rvp controls which will remove butanes from the gasoline during the summer months at a significant economic penalty to the refiners, the TAME operation has the potential to remove 70 to 90 MBPD of the highly reactive 2-Methyl Butenes from the gasoline pool all year round with no economic penalty."

MMT — An Antiknock for Unleaded Gasoline (9)(10)

MMT (methylcyclopentadienyl manganese tricarbonyl) has been used commercially in gasoline as an octane improver since 1957, primarily in leaded gasoline. It has been successfully blended in Canadian unleaded gasoline for many years at the 1/16 gm Mn/gallon level. The antiknock, even at the 1/32 gm Mn/gallon level, could offer close to 1.0 (R+M)/2 octane depending on gasoline composition and octane level. As an additive in U.S. unleaded gasoline, the octane improver could help lower the level of aromatics as well as contribute to reduced gasoline volatility. Table VII can be used to estimate the positive impact on naphtha reforming operations which contributes approximately 34 volume percent of all U.S. gasoline.

MMT was banned by the Clean Air Act amendments of August 3, 1977 for use in unleaded gasoline unless EPA granted a waiver. Subsequently two waiver requests were denied based on studies showing "statistical increases" in hydrocarbon tailpipe emissions from fuels treated with the manganese antiknock. Ethyl Corporation plans to submit a third waiver to EPA during 1990, based on new studies involving a 48-car fleet representing high-volume production vehicles from U.S. manufacturers.

Based on historical data, the use of MMT at low levels in gasoline would probably shift the balance among tailpipe carbon monoxide, nitrogen oxides, and hydrocarbons slightly due to chemical effect on catalyst performance. From an environmental standpoint the risk would seem minor compared to the advantage of reducing overall gasoline volatility and aromatics without capital investment at the refinery. Petroleum refiners will need all the "quality help" they can get as new rules on fuel composition are promulgated by EPA. While the auto makers have traditionally opposed MMT, octane quality from whatever source allows flexibility to increase compression ratio as an aid to meet CAFE (Corporate Average Fuel Economy) requirements. The advantage to the petroleum refiner is obvious when one considers that in a 100,000 barrel gasoline blend, about two 55-gallon drums of MMT can produce the octane equivalent of 5000 barrels of MTBE. (Calculations are based on raising unleaded regular from 87 to 88 ON with 1/32 gm Mn as MMT, octane blending value for MTBE of 108 and no Rvp adjustment.)

In the final analysis it would seem that an antiknock for unleaded gasoline has positive features for the automakers and regulators as well as petroleum refiners.

FUTURE TRANSPORTATION FUEL COMPOSITION

Some long-range estimates of the composition of gasoline, diesel fuel, and their alternatives can be made based on agency environmental targets and early oil industry forays with reformulated gasoline. For several years the EPA and state agencies have studied the environmental impacts of benzene in gasoline, total aromatics in diesel fuel and gasoline, and sulfur in diesel fuel. Gasoline volatility restrictions have been initiated for summer months through Rvp control and limits will become more restrictive in the future. Oxygenated fuels are required in Colorado "front range" cities during winter months to reduce carbon monoxide emissions and similar requirements have spread to critical pollution areas of Arizona, Nevada and New Mexico.

Industry Fuel Reformulation Research Program

In October 1989 three U.S. domestic auto makers and fourteen oil companies announced an extensive joint research and testing program to evaluate a wide range of gasolines. The target is to

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pinpoint fuel composition to reduce emissions, especially ground-level ozone formation. The participants emphasize that the program, as designed, has no bias as to which fuels will be best for air quality.

Participants state that the study is in support of the President's Clean Air Act proposal. However the results may lay the groundwork for a reevaluation of Executive-Branch thinking and possibly redirect some of the emphasis away from methanol as a transportation fuel. The first phase of the study is scheduled for completion by mid-1990. More than likely the date will slip to 1991 because the timing of the initial work is already under pressure.

The first phase involves examination of the emissions, air quality effects and economic relationships-of methanol fuels and methanol fuel blends in prototype vehicles as well as reformulated gasolines in a representation of the current car population. Methanol-fuel vehicles will be specially designed to handle both gasoline and methanol-fuel compositions. Reformulated gasolines comprise various hydrocarbon and oxygenated blends, the latter including ethanol, MTBE and ETBE. All vehicles emissions, exhaust and evaporative, from the program's car/fuel running combinations will be measured and analyzed chemically. This block of information will constitute input to air-quality models to evaluate the effect on potential ozone formation from each car/fuel combination.

The second phase of the program is in the design stage and will use results from the first phase to establish the final targets. Future production vehicles, alternative fuels and reformulated gasolines will generate the basis of this echelon of research. It is entirely possible that the total study will require several years to completion and carry the program well into the 1990 decade.

Emission Control Gasoline

To date three companies have announced reformulated gasolines for specific marketing areas to replace leaded gasoline sold through wide nozzle pumps. ARCO's EC-1 (Emission Control-1) was the first and is marketed in the Southern California area primarily to relieve ground-level ozone formation. Diamond Shamrock and Conoco have introduced special formulations for the Denver area targeted toward carbon monoxide and ground-level ozone. Seasonal adjustments include reduced vapor pressure during the summer and an increase of oxygenates for winter blends.

ARCO's EC-1 Definition (11)

The ARCO EC-1 grade meets ASTM D4814 specifications and typical properties are listed as follows:
- Rvp, Southern California criteria minus 1 psi
- Aromatics, 20 volume percent
- Benzene, 1 volume percent
- Bromine No. 20
- Oxygen, 1 wt.% (min)
- Sulfur, 300 ppm (max)
- Lead below 0.05 gms/gal.

In general, the EC-1 characteristics shown above are close to those that can be expected as agency targets in the 1990 decade. One exception is the 20% level for total aromatics which is too restrictive for the U.S. gasoline pool. EPA targets could ultimately fit in the following ranges for U.S. gasoline: (Also shown in Table VIII)

∘Rvp, 8.0 - 9.0 psi (summer average)
∘Aromatics, 25 - 30 volume percent (max)
∘Benzene, 0.5 - 1.0 volume percent (max) Oxygen, mandatory for some areas.
∘Oxygen, mandatory for some areas.

EPA Limit on Oxygenate Blending

The ultimate concentration for oxygenates in gasoline is probably 3.5 wt. percent oxygen. Gasohol is an exception and is legal to the 3.7 wt. percent limit to allow downstream blending flexibility. It is unlikely that a higher limit would be approved by EPA in the future because nitrogen oxide emissions tend to increase from catalytically controlled vehicles beyond the 3.5 wt. percent level. Based on a 7.5 million barrel per day U.S. gasoline pool, the limit would allow close to 1.5 million barrels of ethers in gasoline. (1)

Diesel Fuel Sulfur and Aromatics (12)

During the mid 1980's there was a good deal of EPA concern about diesel fuel sulfur and aromatics. Regulatory action is pending because sulfur oxides, nitrogen oxides, particulates, and unburned hydrocarbon emissions can all be related to diesel fuel composition. Distillate sulfur and aromatics increased during the past 20 years because of the influx of heavier crudes, more conversion on the fluid cat cracker to make higher octane gasoline, and the increasing demand for distillates that required blending of cracked stocks. Table VIII shows the limits that have been considered by EPA— 0.05 wt. percent sulfur and 20 volume percent aromatics. It is more likely that aromatics will be controlled via cetane index which might allow some flexibility above the 20 volume percent limit. Further, EPA may consider control of distillates a local issue (for example the Los Angeles Basin) and postpone regulatory action on a national scale.

Any restriction on diesel fuel aromatics would be capital intensive because of hydrogen requirements to saturate aromatic rings (12). Because oil industry capital to handle regulatory controls has some limit, action on gasoline composition will top the list. At the same time mandatory reduction of gasoline aromatics would tend to lower cat cracker conversion, which in turn would lower cracked distillate aromatics.

Alternative Fuels

"Alternative Fuels" have been in and out of the news since the oil embargo in the early 1970's. Assuming the definition implies alternatives for "traditional gasoline," the list is as follows:

∘Gasoline blended with oxygenates
∘Methanol
∘Ethanol
∘Natural gas
∘Electricity
∘Solar

Gasoline blended with oxygenates, and specifically ethers, is the "front runner" for 1990. Reformulated gasoline will rely heavily on ethers as the so-called clean-up agent.

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Methanol has been touted by the Bush Administration because hydrocarbon emissions are lower than gasoline whether as M-100 or M-85 (85% methanol and 15% gasoline). However, any significant replacement of traditional gasoline by methanol would require massive outlays of capital for plant construction. Because plants could be situated outside the U.S., there is concern about added exportation of U.S. reliance on energy. Further, there are questions about formaldehyde emissions and safety. (Methanol burns with a colorless flame.) Nevertheless, it is the most likely candidate for fleet operation etc. to gain relief from air pollution in critical areas such as the Los Angeles basin.

Ethanol could play a similar role as methanol with E-100 or E-85 but subsidies would be required for the alcohol to compete economically with current transportation-fuel prices. Ethanol has the unique advantage of being renewable from U.S. agriculture.

Natural gas is currently plentiful in the U.S. and worldwide. Emissions are much lower than gasoline but disadvantages would be difficult to overcome. Tanks must be under relatively-high pressure and vehicles would require more frequent fueling. The most likely application is for fleet operation in critical areas where supply is readily available.

Both electricity and the solar-fuel cell based on hydrogen are long-range prospects for heavily-polluted areas after the turn of the century.

In general it is unlikely that alternatives, aside from oxygenates blended to gasoline, will have much impact on crude-oil-derived transportation fuel in the 1990 decade.

MAINTAINING PRODUCT QUALITY WITH RESTRICTIONS

Two major issues, volatility reduction and aromatics reduction, can be estimated in conjunction with gasoline-pool-octane quality. While each individual refining situation will vary, technical feasibility can be judged by manipulating components in the pool while retaining octane quality.

As pointed out earlier, Table III is a representation of the composition, octane quality, and aromatic content of the 1989 U.S. gasoline pool. By maintaining average octane of 88.4, a reasonable grade mix is available to satisfy the car fleet of the 1990 decade.

Table IX represents a hypothetical U.S. gasoline composition that has been adjusted to reduce summer gasoline Rvp to 9.0 psi and aromatics to a maximum of 30 volume percent. Pool gasoline demand is assumed to average 7.5 MM B/D.

Table IX has been generated from Table III. Comments on assumptions and adjustments are as follows:

○Blending butanes have been reduced 1.5 volume percent from the 1989 gasoline pool —approximately 112,500 B/D. In theory the reduction to 9.0 psi would require the removal of 150,000 B/D of n-butane from gasoline (1).

○The additional pool Rvp reduction accrued from reduced naphtha reformer severity and less conversion on the fluid catalytic cracker, eg less butane make and lower gasoline Rvp from these units which account for over 70 percent of total gasoline to the pool.

○Light straightrun gasoline has been essentially eliminated as a gasoline component because of low octane, which averages 65 (R+M)/2. Disposition was to isomerization where the average octane is increased to 85 (R+M)/2. The higher volatility of the C_5-C_6 isomers is balanced by additional condensation processing (etherification).

∘Aromatics were lowered from 32 to 30 volume percent in the pool, primarily by reducing naphtha reforming severity. This required reducing the octane quality of the reformed gasoline by more than 2 (R+M)/2 octane, but at the same time increased gasoline yield.

∘Pool octane also was lowered incrementally by the loss of 1.5 volume percent blending butanes.

∘Compensating octane was generated by conversion of light straightrun to isomerate, the elimination of direct coker gasoline blending and, most significantly, by the addition of 1.1 volume percent ethers. Ethers to the pool (in exchange for aromatics) preserve the gasoline-blending flexibility required from high-octane components.

∘Lower conversion on the fluid cat cracker reduced gasoline aromatics marginally. It was assumed that the octane quality of the gasoline stream was maintained by taking advantage of both existing and new FCC catalyst technology. Some conversion of isoamylenes to TAME gasoline was assumed to help retain the octane quality of the gasoline stream originating from FCC operations.

∘Alkylate volume to the gasoline pool decreased incrementally due to routing, of more FCC isobutylene to etherification.

The exercise to restrict aromatics in the U.S. gasoline pool indicates that levels below 30 volume percent will be far more difficult to achieve. Aromatics emanate from two sources, reformed and fluid cat cracked gasolines, which comprise over 70 percent of total gasoline. Within the limits of existing technology, high-octane isoparaffins cannot be generated in sufficient volume to replace aromatics. If the integrity of finished-gasoline octane is to be maintained, the reduction of aromatics below 30 volume percent can only be accomplished by the introduction of additional ether or by the use of an antiknock compound for unleaded gasoline. MMT at the 1/32 gm/gal Mn level could add close to 1.0 octane to the unleaded gasoline pool. Eventually this could facilitate the reduction of pool aromatics about 2 additional volume percent (28 volume percent in pool) without loss of octane quality.*

It is unlikely that U.S. gasoline-pool aromatics can be reduced to 25 volume percent in the framework of the 1990 decade without some compromise of marketed gasoline octane quality. Gasoline grades with 20 and 25 volume percent aromatics are being marketed in critical environmental pockets such as Southern California and the Colorado Front Range, but it is at the expense of adjusting other grades and/or exporting aromatics to other marketing areas. The various strategies that seem to be technically feasible for petroleum refining to control aromatics in gasoline within the decade are outlined as follows:

∘Reduction of total aromatics in the U.S. gasoline pool to 30 volume percent or to 28 volume percent with an EPA waiver for MMT, the manganese antiknock is possible. Octane quality

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* MMT response is less effective with aromatic hydrocarbons. The octane return from a given amount of MMT should increase as aromatics are withdrawn from the gasoline pool.

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could be maintained and the target might be achieved by 1995. Further reduction of total aromatics while holding current quality (Table III) would require an extensive petroleum refining move to etherification by the latter part of the decade.

•Assuming all marketed grades were reduced to an average of 87 octane (Table III all unleaded regular) aromatics could be reduced to about 27 volume percent or to 25 volume percent with an EPA waiver for MMT.

•Special gasolines containing 20-25 volume percent aromatics could be blended for critical pollution areas. "Excess aromatics" would either appear in other grades or be exported for use outside the regulated area. Current quality could be maintained. This appears to be the present oil industry approach with today's emission control fuels.

•An alternative to the control of total aromatics in all U.S. gasoline would be to shift regulatory targets to specific aromatics such as benzene and the photochemically reactive heavy aromatics such as xylenes. While this would require extensive processing and separation facilities within petroleum refining, it is possible that a higher level of environmental benefit could be achieved while maintaining current octane quality. Further study is indicated.

IMPACT ON PETROLEUM REFINING

The oil industry will require extensive capital investment for processing as well as adequate lead time to further reduce volatility and limit aromatics in U.S. gasoline. Aromatic reduction, whatever course it takes by regulatory agencies, has the greatest potential impact to gasoline-octane quality. The outlook is for continued attrition of small refineries and independent refiners in the U.S., a trend that commenced in the early 1970's with the oil embargo and accelerated with the lead phasedown. Because of the need for capital to handle fuel-regulatory requirements, foreign interest in U.S. refining will continue to rise. Further, if gasoline quality cannot be maintained from domestic refining sources, high-octane blendstocks and feedstocks will be imported in increasing quantities.

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Table I

AVERAGE 1989 U.S. GASOLINE POOL (1)+

APPROXIMATE COMPOSITION, OCTANE AND AROMATICS

	Volume Percent	Octane Range*	Aromatics Range
Blending Butanes	7.0	91-93	---
Light Straightrun	3.3	55-75	0-4
Isomerate	5.0	80-88	---
Cat Cracked	35.5	84-89	23-33
Hydrocracked	2.0	85-87	2-6
Coker	0.6	60-70	4-8
Alkylate	11.2	90-94	---
Reformate **	34.0	86-96	50-80
MTBE	1.4	106-110	---
Total	100.0		
Average Octane*		88.4	
Average Aromatics			32.1

+ Does not include downstream blending
* (R+M)/2 octane clear
** Includes BTX blending

Table II

U.S. GASOLINE GRADE MIX (1)
1988 Estimate

Grade	Approximate Volume Percent	(R+M)/2 Octane
Unleaded Premium	25	92
Unleaded Midgrade	8	89
Unleaded Regular	50	87
Leaded Regular	17	89 (88 clear)
Total	100	
Average (Clear)		**88.6**

Table III

U.S. GASOLINE GRADE MIX
1989 Estimate

Grade	Approximate Volume Percent	(R+M)/2 Octane
Unleaded Premium	22	92.5
Unleaded Midgrade	8	89
Unleaded Regular	60	87
Leaded Regular	10	89 (88 clear)
Total	100	
Average (Clear)		**88.5**

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Table IV

OCTANE BLENDING VALUES AND BOILING POINTS OF GASOLINE AROMATICS (4)

Aromatic	Research	Motor	(R+M)/2	Boiling Pt.°F
Benzene	106	88	97	176
Toluene	114	93	103.5	231
p-Xylene	120	98	109	281
m-Xylene	120	99	109.5	282
o-Xylene	105	87	96	291
Ethylbenzene	114	91	102.5	277
C_9 Aromatics	117	98	107.5	-
C_{10} Aromatics	110	92	101	-

Table V

Atmospheric Reactivity and Vapor Pressure(5)

(Hydrocarbons and Oxygenates)

Compound	Atmospheric Reactivity*	Blending Rvp, psi**
n-Butane	2.7	60
Isopentane	3.6	21
n-Pentane	5.0	16
Isohexane	5.0	7
n-Hexane	5.6	5
Benzene	1.3	3
Toluene	6.4	0.5
M-xylene	23.0	0.3
Butene-1	30.0	65
Butene-2	65.0	50
Pentene-1	30.0	16
2-Methyl 2-Butene	85.0	15
2-Methyl 1-Butene	70.0	19
Methanol	1.0	60
Ethanol	3.4	18
MTBE	2.6	9
ETBE	8.1	3-5
TAME	7.9	1-2

* Gas phase reaction rate with the hydroxyl (OH) radical.

** Values will vary with blendstocks.

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Table VI

OCTANE AND VOLATILITY CHARACTERISTICS OF SELECT OXYGENATES (1)

	Blending Octane			Blending Rvp, psi*	Boiling Point °F
	RON	MON	(R+M)/2		
Methanol	133	99	116	58-62	149
Ethanol	130	96	113	18-22	172
MTBE	118	100	109	8-10	131
ETBE	118	102	110	3-5	158
TAME	111	98	104.5	1-2	187

* Can vary with the hydrocarbon composition of gasoline.

Table VII

NAPHTHA REFORMING (6)
OCTANE NUMBER vs AROMATICS AND VOLATILITY

Severity, RON clear	90	95
(R+M)/2 octane number*	86.0	90.1
Gas Yield, scf/bbl chg		
Hydrogen	967.0	1015
Methane	55	73
Ethane	55	71
Liquid Yield, vol.%		
Propane	3.6	4.9
Isobutane	1.8	2.4
n-Butane	2.5	3.4
Pentanes Plus	85.6	81.9
Rvp, psi	2.7	3.1
Aromatics, vol.%*	47	55

* Estimated from average industry data.

Table VIII

ESTIMATED COMPOSITION FOR
TRANSPORTATION FUEL REGULATORY TARGETS

Gasoline

Rvp, 8.0-9.0 psi (summer average)
Aromatics, 25-30 vol.% (max)
Benzene, 0.5-1.0 vol.% (max)
Oxygen, mandatory for some areas
Olefins, (Br No. and/or C_5 olefin limit)

Diesel Fuel

Sulfur, 0.05 wt.% (max)
Aromatics, 20 vol.% (max)

Note: Aromatic control for gasoline composition could
specifically target photochemically reactive ring
compounds. Aromatic control for diesel fuel would be
via minimum cetane index.

Table IX

AVERAGE U.S. GASOLINE POOL
(Adjusted for 9.0 psi Summer Rvp and 30 vol.% Aromatics)

ESTIMATED COMPOSITION, OCTANE, AND AROMATICS

	Volume Percent	Octane Range *	Aromatics Range
Blending Butanes	5.5	91-93	---
Light Straightrun	1.0	55-75	0-4
Isomerate	8.0	82-88	---
Cat Cracked	35.0	84-89	20-29
Hydrocracked	1.5	85-87	2-6
Alkylate	11.0	90-94	---
Reformate **	35.5	83.5-94	42-78
Ethers	2.5	106-110	---
Total	100.0		
Average Octane*		88.4	
Average Aromatics			30.0

* (R+M)/2 octane clear
** Includes BTX blending

Environmental
Science & Technology

Catalysis of NO Decomposition by Mn_3O_4

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Catalysis of NO Decomposition by Mn₃O₄

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□ A flow reactor and chemiluminescent NO_x analyzer were used to measure the rate of decomposition of NO catalyzed by Mn_3O_4 in purified air at atmospheric pressure. The decomposition is first order in NO with Arrhenius parameters of E_{app} = 12.4 ± 0.2 kcal mol⁻¹ and ln A(s) = 9.29 ± 0.24. Because Mn_3O_4 is the primary Mn-containing combustion product of the fuel additive methylcyclopentadienylmanganese tricarbonyl (MMT), the catalytic properties of Mn_3O_4 should be considered in evaluating the potential air quality problem posed by MMT.

The effects of methylcyclopentadienylmanganese tricarbonyl (MMT) on automotive emissions and air quality have attracted recent attention (1–5). MMT has been used commercially as an antiknock additive for unleaded gasoline. In limited amounts, MMT may be compatible with lead-sensitive automotive emission control devices. Additionally, MMT is currently used as a combustion improver and smoke inhibitor in fuel oil. Because of the toxic properties of manganese compounds, a National Academy of Sciences panel recommended objective evaluation of the potential air quality problem associated with increasing use of Mn-containing fuel additives (1).

The present investigation is concerned with the heterogeneous catalysis of NO decomposition by Mn_3O_4, the primary Mn-containing combustion product of MMT (2, 4). Tests with both simulated (4) and actual (5) automotive exhaust indicate that MMT can profoundly affect emissions. Several mechanisms have been suggested for observed decreases in NO emissions when MMT is added to gasoline. These include suppression of NO formation during combustion, catalysis of NO reduction by CO, and catalysis of NO decomposition. The purpose of this preliminary communication is to report the rapid catalytic decomposition of NO by Mn_3O_4 under conditions which exclude potentially confounding effects due to other reactions.

Despite favorable thermodynamic considerations, the rate of the homogeneous decomposition of NO to N_2 is very slow below 1000 °C (6). Activation energies reported for the homogeneous decomposition range from 64 to 86 kcal mol⁻¹. Although the study did not include Mn_3O_4, Shelef et al. (7) identified several metal oxides as catalysts for the heterogeneous decomposition with apparent activation energies ranging from 11 to 33 kcal mol⁻¹. Due to very low preexponential factors, however, these catalysts were judged unsuitable for practical decomposition of NO formed in combustion
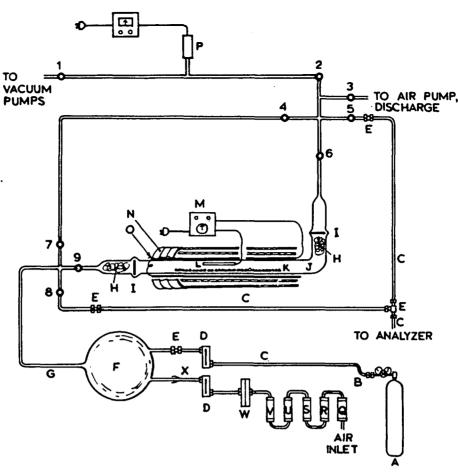
processes. Moreover, inhibition by O_2 was observed in some cases. The catalytic activity of Mn_3O_4 toward NO in the presence of O_2 is therefore of potential interest in air pollution control, in addition to the need for information on the effects of MMT.

Experimental

The flow reactor shown schematically in Figure 1 was used to measure the rate of catalyzed NO decomposition in purified air as a function of temperature. NO was introduced into the air carrier gas at atmospheric pressure from a cylinder of 6.2 ± 0.1 ppm of NO and 0.3 ± 0.1 ppm of NO_2 in N_2 supplied by B.O.C. Special Gases (U.K.). Introduction of atmospheric constituents which might confound the experiment was prevented by passing laboratory air through a five-canister purification train followed by a particulate filter (Figure 1). The NO flow rate was varied from 102 to 620 cm³ min⁻¹ in approximately 100 cm³ min⁻¹ increments to give 6 inlet NO concentrations ranging from approximately 0.2 to 1.2 ppm at each of 4 temperatures. A mechanical pump was used to draw the gases through the reactor at a constant combined flow rate of 3.2 L min⁻¹. Flow meters were calibrated with air at 25 °C.

The reactor was a 2.5-cm i.d. L-shaped Pyrex tube fitted with high-vacuum O-ring seals. This configuration facilitated removal of the reactor for charging with Mn_3O_4 following measurements in the absence of sample, e.g., blank determinations. After initial pumpdown with oil diffusion and mechanical vacuum pumps, the system was found capable of maintaining a steady pressure of approximately 1×10^{-4} Torr, the lower detection limit of the Pirani gauge. The temperature in the center of the 0.262-L reaction zone containing Mn_3O_4 was maintained within ±0.5 °C of each setting by a Pye Ether 1793B/10 electronic controller and insulated heating tape. The controller was calibrated with a Comark electronic thermometer with the probe placed inside the reactor with air flowing at 3.2 L min⁻¹. Measurement of the temperature at various positions within the reaction zone showed that temperature differences did not exceed 2 °C.

Gas mixtures entering and leaving the reactor were analyzed for NO and NO_2 with a Thermo Electron Model 14D chemiluminescent NO–NO_2–NO_x analyzer. The analyzer was calibrated with a standard sample of NO and NO_2 in N_2 and cross-checked for NO_2 with a gas permeation tube apparatus previously calibrated by a gravimetric technique. The instrumental calibration was rechecked before and after concentration measurements at each temperature. The calibration was found essentially drift-free; concentration mea-

A. NO-in-N$_2$ Cylinder
B. Regulator and Valve
C. Teflon Tubing
D. Rotometer
E. Swagelok Coupling
F. Pyrex Mixing Chamber
G. Pyrex Tubing
H. Glass Wool
I. O-Ring Coupling
J. 2.5cm ID Reactor
K. Mn$_3$O$_4$
L. Fe/Con Thermocouple Probe
M. Pye Controller

N. Asbestos Insulation
O. Heating Tape
P. Pirani Gauge, Indicator
Q. Desiccant
R,S. Activated Charcoal
U. 13x Mol. Sieve
V. 5A Mol. Sieve
W. Glass Fibre Filter
X. Tygon Tubing
1-9. Vacuum Stopcocks

Figure 1. Schematic diagram of apparatus

surements were reproducible within 0.01 ppm.

Mn$_3$O$_4$ was prepared by heating reagent-grade MnO$_2$ (B.D.H. Chemicals Ltd.) in air for 3 days at 1000 °C (8). X-ray diffraction analysis confirmed the formation of Mn$_3$O$_4$ and the absence of any other crystalline phases; both d spacings and relative intensities were in good agreement with accepted values (9). The material produced by this method is heterogeneous in appearance and consists of predominantly coarse, dark brown particles flecked with smaller purplish-black particles. The powder patterns for the two types of particles

were indistinguishable, however. A very crude estimate of the specific surface area was made by sieving the sample into four size categories. Assuming cubic geometry and using the bulk density of 4.86 g cm^{-3} yield the estimate of 0.005 m^2 g^{-1}, probably a minimum value. Following determination of the system blanks, the reactor was charged with 4.03 g of Mn$_3$O$_4$ distributed evenly throughout the reaction zone.

Blank determinations in the absence of Mn$_3$O$_4$ were made at temperatures from 30 to 243 °C over the NO concentration range of 0.2–1.2 ppm. NO$_2$ concentrations ranged from 0.04

Table I. Kinetic Data

215 °C		223 °C		234 °C		243 °C	
c_i, ppm	c_e, ppm	c_i, ppm	c_e, ppm	c_i, ppm	c_e, ppm	c_i, ppm	c_e, ppm
0.23	0.20	0.24	0.20	0.23	0.19	0.21	0.16
0.45	0.37	0.46	0.38	0.42	0.32	0.41	0.30
0.59	0.51	0.62	0.50	0.58	0.46	0.57	0.42
0.76	0.67	0.76	0.63	0.78	0.60	0.78	0.57
0.86	0.75	0.92	0.77	0.90	0.70	0.90	0.65
1.09	0.92	1.10	0.95	1.11	0.85	1.06	0.80
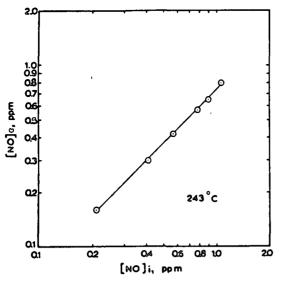
Figure 2. Comparison of inlet and exit NO concentrations at 243 °C

Figure 3. Arrhenius plot

to 0.10 ppm. For each flow setting, inlet and outlet NO concentrations were identical at all temperatures. NO_2 concentrations were similarly unchanged. Observed NO and NO_2 concentrations could be computed solely on the basis of dilution of the NO–NO_2 source with the carrier gas. These observations demonstrate that within the temperature range studied, surfaces of the apparatus in contact with the gas mixture were inactive toward NO and NO_2. The reactor was then charged with Mn_3O_4 and pumped down with heating for 5 days to degas the system.

The determinations were repeated with Mn_3O_4 in the reactor. The steady-state NO concentrations are given in Table I and shown graphically in Figure 2 for 243 °C. Outlet NO concentrations are lower than inlet NO concentrations; the difference increases with increasing temperature. The linear relationship between the logarithms of the inlet and outlet NO concentrations is significant in terms of subsequent analysis of the kinetic data. At each temperature, inlet and outlet NO_2 concentrations were identical at each flow setting and unchanged with respect to values measured in the blank determinations.

Data Analysis

Evaluation of the kinetic parameters for the heterogeneous decomposition of NO according to:

$$NO(g) = 0.5N_2(g) + 0.5O_2(g)$$

is based upon application of the Arrhenius equation to the integrated rate law for a plug flow reactor (10). In general, the NO decomposition rate is given by:

$$\frac{dC}{dt} = -kC^n \tag{1}$$

where C is the NO concentration, t is time, k is the heterogeneous rate constant, and n is the reaction order. The order n can be obtained from a plot of log (dC/dt) as a function of log C for various inlet concentrations of NO. In this case, $n = 1$ and the integrated rate law for the flow reactor becomes:

$$-k\frac{V}{u} = \ln\frac{C_e}{C_i} \tag{2}$$

where u is the volume flow rate, V is the reactor volume, and C_e and C_i are the steady-state exit and inlet NO concentrations, respectively. The linearity of log C_e as a function of log C_i at each temperature confirms the applicability of the plug flow reactor model for the temperature range of this study. In each case, the slope is unity, a further confirmation of the
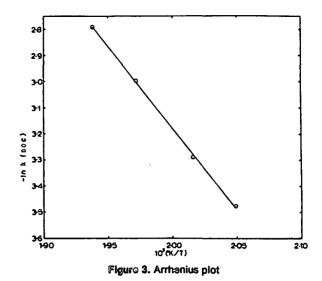
Table II. Temperature Dependence of Rate Constant

T, °C	k, s⁻¹	T, °C	k, s⁻¹
215	0.0309	234	0.0499
223	0.0373	243	0.0613

applicability of the first-order integrated rate law for the flow reactor. Values of k given in Table II were computed from Equation 2 using the data in Table I.

The Arrhenius parameters were evaluated on the basis of:

$$\frac{d\ln k}{dT} = \frac{E_{app}}{RT^2} \tag{3}$$

where E_{app} is the apparent activation energy, T is the absolute temperature, and R is the gas constant. In integrated form, the Arrhenius equation may be written:

$$k = A \exp(-E_{app}/RT) \tag{4}$$

where A is the temperature-independent preexponential factor for the temperature range of this study. As shown in Figure 3, the Arrhenius plot of ln k as a function of $1/T$ is linear with $E_{app} = 12.4 \pm 0.2$ kcal mol⁻¹ and ln A(s) = 9.29 ± 0.24. The uncertainties are given in terms of the 90% confidence intervals (11).

Discussion

The results demonstrate that Mn_3O_4 can accelerate the decomposition of NO in purified air at moderate temperatures. The observed reaction order of 1 is consistent with many previous studies of the catalyzed decomposition of NO. The apparent activation energy of 12.4 kcal mol⁻¹ is lower than most previously reported values for other catalysts but comparable to values of 10.6 and 13.2 kcal mol⁻¹ for two catalysts studied by Shelef et al. (7). The preexponential factor for the Mn_3O_4-catalyzed decomposition of NO, however, is much larger than values reported for other catalysts by Shelef et al., who compared NO decomposition rates on the basis of mol m⁻² min⁻¹ at 500 °C and 1 atm. Extrapolation of the present data to these conditions results in an NO decomposition rate several orders of magnitude faster than rates reported previously for other catalysts. The possible practical application of this finding is a subject for continuing study.

With regard to the MMT issue, these findings suggest the possibility of a beneficial effect, namely, a decrease in NO_x emissions, and may help to explain such effects in tests with MMT under simulated automotive exhaust conditions (4). However, extrapolation to either actual automotive exhaust

or the atmosphere would be premature in the absence of more extensive tests. Nevertheless, these findings indicate that in evaluating the potential air quality problem posed by MMT, the catalytic activity of MMT combustion products should be considered, in addition to increases in atmospheric Mn concentrations.

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Appendix 10

APPENDIX 10

THE SLIGHT INCREASE IN HYDROCARBON EMISSIONS IN TEST VEHICLES USING THE HiTEC 3000 ADDITIVE IS NOT MATERIAL TO THIS WAIVER APPLICATION

I.   INTRODUCTION

The data from Ethyl Corporation's ("Ethyl") 48-car test fleet show a very small, but statistically detectable, increase in hydrocarbon ("HC") emissions for the test vehicles using the HiTEC® 3000 Performance Additive (the "Additive"). For the first 50,000 miles, HC emissions in those vehicles increased 0.018 gpm on average. Over 75,000 miles, the small increase in HC emissions ranged, on average, from no higher than 0.018 gpm to as low as 0.010 gpm, depending upon the method of interpreting the test data. This Appendix presents additional information that shows that the small increase in HC emissions is not material to a decision on this waiver application.

II.   THE CAPABILITY TO DETECT STATISTICALLY A CHANGE IN AUTOMOTIVE TAILPIPE EMISSIONS IS A FUNCTION OF THE DESIGN OF THE TEST PROTOCOL; STANDING ALONE, A STATISTICALLY DETECTABLE CHANGE IN EMISSIONS HAS NO BEARING ON THE PRACTICAL IMPORTANCE OR MATERIALITY OF THE CHANGE.

Whether a change in tailpipe emissions will be statistically detectable (i.e., statistically significant) is simply a function of the design of the test protocol. As the number of cars tested increases, and the mileage intervals at which emissions tests occur increases, the magnitude of any difference in emissions that can be detected statistically decreases. In other words, smaller and smaller differences in emissions become statistically detectable as the size of the test fleet and the number of test intervals increases.

- 2 -

The ability to detect statistically small differences in emissions does not necessarily mean, however, that the detected differences have any "practical," real world importance, as the following example illustrates. Assume Companies "A" and "B" both manufacture a similar cereal (e.g. corn flakes) and sell the cereal in nominal 20 ounce boxes. Assume also that four boxes of each company's cereal are weighed using a very precise set of scales. The hypothetical weights and deviation from means are shown below:

Box No.	Box Weight "A"	Box Weight "B"	Deviation from Means "A"	Deviation from Means "B"
1	20.01	20.05	0.00	-0.02
2	19.99	20.08	-0.02	0.01
3	20.02	20.09	0.01	0.02
4	20.02	20.06	0.01	-0.01
Means	20.01	20.07	---	---

The standard error based on this hypothetical example is approximately 0.012. The two means in the example (20.01 and 20.07) thus differ by about 5 standard errors (0.06/.012) which, applying standard t-tables, is statistically "detectable" (i.e., significant). Whether that difference has any "practical" importance, however, requires the aid of a different discipline (e.g., economics) where the question might become, for example, would consumers prefer Company B's cereal because they get 0.06 more ounces per box? The answer to a question such as that cannot be answered statistically.

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Because of the careful design of Ethyl's 48-car test program, statisticians are able to detect very small differences in tailpipe emissions, such as the slight increase in HC emissions for the Additive-fueled test cars. This detection ability, however, does not mean that the emissions difference -- like the difference in the weights of the cereal boxes -- is of any practical importance. Instead, other considerations become relevant, and, as discussed below, they show that the small HC emissions increase attributable to the Additive in the test fleet is not material to a decision on this waiver application.

A.   In Commercial Operation, the Additive Will Not
      Affect HC Emissions.

To isolate the Additive's effect on tailpipe emissions, Ethyl used a base fuel (Howell EEE) with and without the Additive in its test program. This resulted in test fuels having unequal octane levels, with the fuel containing the Additive having a higher (by about one octane number) octane rating. This octane imbalance is important because the octane enhancing characteristic of the Additive will allow refiners to reduce the aromatic content of unleaded gasolines without sacrificing octane.[1] This, in turn, will reduce HC tailpipe emissions, an

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[1]   See Appendix 6, at 3. This reduction in aromatics has been estimated to fall anywhere between 1.2 and 2.0 percentage points of the gasoline by volume (e.g., from 31.2 percent of the fuel by volume to 30 percent or lower). Id.

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effect not reflected in Ethyl's test fleet data.[2/] Such a
reduction would offset the small HC emissions increase exhibited
in the test fleet.

One independent study, for example, indicates that
decreasing aromatics from 35 percent to 30 percent of the volume
of unleaded gasoline reduces HC emissions by 22 percent, or 4.4
percent for each percentage point decrease in the fuel's aromatic
content.[3/] The 1.2 to 2.0 percentage point decline in the volume
of aromatics attributable to use of the Additive, therefore,
would result in about a 5 to 9 percent decline in total HC
exhaust emissions.

SAI calculated the mean integrated HC emissions for the
Additive-fueled cars in Ethyl's test fleet to be 0.281 gpm for
the first 50,000 miles of vehicle operation. Thus, a 5 to 9
percent reduction in HC emissions translates into a reduction in
HC emissions for the Additive-fueled cars of somewhere between
0.014 gpm and 0.025 gpm.[4/] Such a decrease in HC emissions would

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[2/]   See Appendix 9, at Attachments 9-1, 9-2 and 9-3.

[3/]   See id. at Attachment 9-2.

[4/]   For 75,000 miles of vehicle operation, SAI calculated the
mean integrated emissions for the Additive-fueled vehicles to be
0.307 gpm. See Appendix 2A, at D-25. The 5 to 9 percent
reduction noted above translates into a 0.015 to 0.028 gpm HC
emissions reduction for the Additive-fueled vehicles over the
full 75,000 miles of vehicle operation.

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generally offset the very small HC emissions increase exhibited in the test fleet.

A second independent study reaches essentially the same conclusion.[5] This study, conducted by General Motors, shows that a decrease in the aromatic content of unleaded fuel from 49 percent to 31 percent by volume reduces HC emissions by 0.21 gpm. A reduction of this magnitude translates into a HC reduction of approximately 0.0116 gpm for each percentage point decrease in aromatics. A 1.2 to 2.0 percent drop in aromatics, therefore, corresponds to a HC emissions reduction up to 0.023 gpm, a reduction sufficient to generally offset the slight HC emissions increase exhibited in Ethyl's test fleet.

Indeed, speciation testing completed by Ethyl on cars from the test fleet using fuels with equivalent octane ratings (obtained by adding a small amount of mixed xylenes and the HiTEC 3000 additive to various unleaded fuels) indicates that use of the Additive does not increase total HC emissions.[6] The results of this speciation testing show that HC emissions from the car using the Additive were generally the same as -- and in some cases were less than -- those from the car using the base fuel with the added xylenes.[7] For these reasons, the small HC

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[5]   See Appendix 9, at Attachment 9-1.

[6]   See Appendix 4, at Attachment 4-8.

[7]   Id.

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emission increase exhibited in the test fleet by the cars using

the Additive should not occur in commercial operation.

B.   The Small HC Increase Does Not Cause or Contribute to
        the Failure of Vehicles to Meet Emission Standards.

Leaving aside the likely reduction in gasoline aromatics

made possible by use of the Additive in commercial operations,

Ethyl has established conclusively that the Additive does not

cause or contribute to the failure of emission control devices or

systems to meet the existing HC emission standard.[8/] Indeed,

Ethyl has shown that use of the Additive will not cause or

contribute to the failure of emission control devices or systems

to meet the stricter HC emission standards likely to be

established by Congress for application in the mid-1990's.[9/]

That the Additive will not cause or contribute to the

failure of emission control devices is further confirmed by an

analysis which considers what effect use of the Additive would

have in the certification process mandated by the Clean Air Act

("Act") for new motor vehicles.[10/] This analysis shows that the

prototypes for each of the car models used in Ethyl's test

program would have been certified as complying with the

[8/]   See Appendix 2A, at 54-55.

[9/]   See Appendix 11.

[10/]   Section 206 of the Act requires EPA to test new motor
vehicles and engines to certify compliance with the emission
control standards for mobile sources established under § 202 of
the Act. See 42 U.S.C. § 7525.

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applicable HC emission standard <u>even if operated on fuel</u>
<u>containing the Additive.</u>[11/] In light of these test results, the
slight HC emission increase exhibited from the cars in the test
fleet using the Additive cannot be deemed to be material to a
decision on this waiver application.

    C.   The Small Increase in HC Emissions Occurred
             Within the First 4000 Miles of Vehicle Operation
             <u>and Did Not Increase Thereafter.</u>

The statistically significant increase in HC emissions
attributable to the Additive occurs within the first 4000 miles
of vehicle operation (i.e., 1000 to 5000 miles) using the
Additive.[12/] SAI calculates this initial difference to be 0.017
gpm. Thereafter, mean integrated emissions, measured from the
emission levels at the 5000 mile test interval for the two test
fuels, are statistically indistinguishable through 75,000 miles.
In fact, HC emissions from cars using the Additive may actually
decline relative to clear-fuel vehicles in the 50,000 to 75,000
mile interval -- i.e., mean integrated emissions for the full
75,000 miles of vehicle operation <u>range</u> from no higher than 0.018
gpm to as low as 0.010 gpm.[13/]

[11/]   <u>See</u> Appendix 2A, at 48-49.

[12/]   <u>See id.</u> at 42-44.

[13/]   <u>Id.</u> at D-31. The variation in average HC emissions levels
depends upon how the test data is interpreted. <u>Id.</u> at 13-14.

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Together, these analyses establish that any HC emissions effect attributable to the Additive is quite limited, and that there is no deteriorative impact on emissions after the first 4000 miles.

D.   The Small HC Increase Associated with Use of the Additive is Not Material in Light of the Variability in HC Emissions Among Vehicle Models in the Test Fleet.

An analysis of the test data from Ethyl's test fleet shows that the composition of the fleet and the choice of vehicle models has a far greater impact on HC emissions than the type of fuel used to operate the vehicle. A graph of individual car model HC emissions from Ethyl's test fleet is shown in Attachment 10-1 and illustrates the large variability in car model HC emissions.[14]

The car model effect is further highlighted by subdividing the fleet into "high" and "low" emitter classes. Cars that exceeded the 0.41 gpm HC standard within the first 50,000 miles of vehicle operation are classified as "high" emitters (models D, F and T) and the remaining cars are classified as "low" emitters. The clear fuel HC emissions averaged 0.420 gpm and 0.186 gpm for the "high" and "low" emitters, respectively.[15] This difference

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[14]   Attachment 10-1 is produced in SAS/GRAPH® Release 6.03 version using the total ETHYL4S2 dataset and quadratic curve representations in the SAS® procedure GPLOT.

[15]   See Attachment 10-2.

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of 0.234 gpm exceeds by a factor of 13 the very small HC emission increase attributable to use of the HiTEC 3000 additive.

Moreover, even if the analysis is limited to the "low" emitters, the variation in HC emissions is still substantial. For example, HC emissions averaged 0.129 gpm for clear-fuel Model G cars.[16/] By contrast, HC emissions averaged 0.271 gpm for clear-fuel Model H cars.[17/] The difference in average HC emissions between these models, 0.142 gpm, is almost 8 times larger than the small HC emissions increase associated with use of the Additive in the test program.

What this means as a practical matter is that variations in the composition of the automotive fleet from year-to-year have a far more significant effect on HC emissions than any possible effect attributable to use of the Additive in unleaded gasoline.

E.   The Small HC Emission Increase Will Not Adversely Affect Ambient Ozone Concentrations.

When Congress, in 1965, first directed that an emissions standard be established under the Clean Air Act ("Act") to control HC emissions, its major concern with automobile emissions was the formation of ozone, "a highly poisonous variety of oxygen."[18/] Congress reaffirmed this concern when it amended the

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[16/]   Id.

[17/]   Id.

[18/]   1965 U.S. Code Cong. & Admin. News 3608, 3611.

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Act in 1970, and again in 1977.[19] In light of this clear

congressional concern that HC emissions contribute to the

formation of ozone, Ethyl requested Systems Applications, Inc.

("SAI") to apply the Urban Airshed Model to predict the impact of

using the Additive on ambient ozone levels.

The results of SAI's analysis establish that use of the

HiTEC 3000 additive will not adversely affect ambient ozone

levels.[20] To the contrary, use of the Additive could have a

slight beneficial effect on ambient ozone concentrations.

Because of the substantial reductions in automotive NOx emissions

that occur when using the Additive, its use could marginally

reduce peak ozone levels in some areas, as well as reduce the

population's exposure to such peak ozone levels.[21] That the

small HC emission increase exhibited in the test data does not

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[19]   See, e.g., A Legislative History of the Clean Air Amendments
of 1977 (Comm. Print, Senate Comm. on Env't and Public Works
1978) at 746 ("Hydrocarbons emitted into the air from automobiles
react with nitrogen oxides. . . in the atmosphere to form
photochemical oxidant -- smog. . . . There is general agreement
that the 0.41 hydrocarbon standard should be imposed as rapidly
as possible to mitigate the pervasive smog problem." (Statement
of Senator Muskie (D-MA)).

[20]   See Appendix 5.

[21]   Id. at 51-63. In addition to the absence of an adverse
impact on ozone formation, use of the Additive will actually
result in a significant reduction in total pollutant emissions.
Ethyl estimates, that by 1999, total pollutant emissions from
automotive sources using the Additive would fall by almost 1.7
billion pounds per year even if the very small HC increase should
occur in commercial operation. See Appendix 7.

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adversely affect ozone formation further illustrates that the

very small HC increase is of no practical importance.
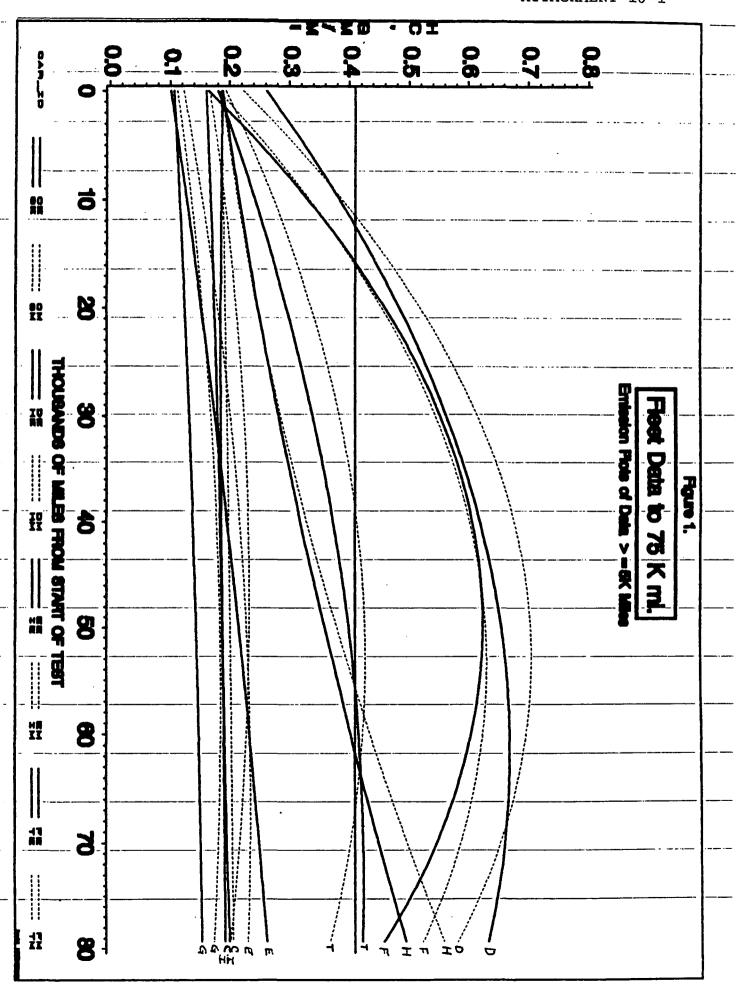
III. CONCLUSION

In summary, this Appendix has shown that the slight HC

emissions increase exhibited for the vehicles using the Additive

in Ethyl's test fleet has no practical importance because:

> (1) A statistically detectable change in
> emissions, standing alone, has no bearing on
> the practical importance or materiality of
> the change. The capability to detect
> statistically a change in automotive tailpipe
> emissions depends solely on the design of the
> test protocol. Because of the extensive
> nature of the testing completed by Ethyl in
> its test program, very small changes in
> tailpipe emissions can be detected, even
> though as a practical matter, they are
> unimportant.
>
> (2) In commercial use, the Additive will
> allow refiners to reduce the aromatic content
> of unleaded gasoline without sacrificing
> octane. This, in turn, will reduce HC
> tailpipe emissions, offsetting the small HC
> emissions increase exhibited in the test
> program;
>
> (3) Even if the small HC emissions increase
> is manifested in commercial operations, use
> of the Additive will not cause or contribute
> to the failure of emission control devices or
> systems to meet the existing or probable
> future HC emission standards. Indeed, the
> prototypes of each of the car models used in
> the test fleet would have been certified
> under the Clean Air Act as complying with the
> applicable HC emission standard even if
> operated on a fuel containing the Additive;
>
> (4) The small HC emissions increase in the
> test program occurred within the first 4000
> miles of vehicle operation. Thereafter, HC

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emissions from cars using the Additive did
not increase relative to the clear-fuel cars;

(5)   The test data shows that a consumer's
choice of car model has a potentially far
more significant impact on HC emissions than
any possible effect attributable to use of
the Additive; and

(6)   Use of the Additive will not adversely
affect ambient ozone concentrations.

For the reasons noted above, the very small, but
statistically detectable, HC emissions increase exhibited for the
vehicles using the Additive in the test fleet are not material to
a decision on this waiver application.

Figure 1.

Fleet Data to 75 K mi.
Emission Plot of Data > =6K Miles

THOUSANDS OF MILES FROM START OF TEST

INTEGRATED AVERAGE HYDROCARBON CLEAR-FUEL EMISSIONS
FOR 1-50K MILES BASED ON APPENDIX 2B, TABLE 2-3A

CAR MODEL	EMISSIONS (GM/M)
High Emitters	
D	0.469
F	0.478
T	0.314
Total	1.261
Average	0.420
Low Emitters	
C	0.175
E	0.168
G	0.129
H	0.271
I	0.185
Total	0.928
Average	0.186

Appendix 11

APPENDIX 11

THE IMPACT OF THE HITEC 3000 PERFORMANCE ADDITIVE
ON COMPLIANCE WITH FUTURE EMISSION STANDARDS

I.   INTRODUCTION

The emission standards to which the Agency must look in making a determination on Ethyl's waiver application are the existing standards under the Clean Air Act ("Act"). In this regard, Ethyl has shown, through its test program, that the HiTEC® 3000 Performance Additive (the "Additive") does not cause or contribute to the failure of emission control devices or systems to meet existing emission standards.

However, Congress is currently considering amendments to the Act, including stricter emission standards for mobile sources that would become effective in the mid-1990's. This Appendix will show that use of the Additive will not cause or contribute to the failure of automobiles to meet the stricter emission standards currently under congressional consideration.

II. PROTOCOL FOR THE ANALYSIS

To determine how the Additive would affect compliance with potential future emission standards, Ethyl requested Systems Applications, Inc. ("SAI") to conduct a statistical analysis of the Ethyl test data applying, as appropriate, statistical analyses similar to those described in Appendix 2A. The general parameters of these analyses are summarized below.

A.   Future Emission Standards

Absent enactment of amendments to the Act, any discussion of future emission standards is by necessity somewhat speculative. Nevertheless, this analysis required SAI to apply emission

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standards applicable to future model year vehicles. SAI applied a set of two-tiered standards in this analysis on the assumption that amendments to the Act would extend the useful life of automobiles, and would require compliance with two different sets of standards depending upon the age or mileage of the vehicle. For the first five years or 50,000 miles ("5/50") of vehicle operation, one set of standards would apply, followed by a somewhat less stringent standard for the next 5 years or 50,000 miles ("10/100").

For hydrocarbons ("HC"), SAI assumed the 5/50 standard would be 0.31 grams per mile ("gpm") for total HC emissions, and 0.25 gpm for non-methane HC emissions. The 10/100 standard for HC would be 0.39 gpm for total HC emissions, and 0.31 for non-methane HC emissions. With respect to nitrogen oxide ("NOx") emissions, SAI assumed the 5/50 standard would be 0.4 gpm, to be followed by a 10/100 NOx standard of 0.5 gpm. For carbon monoxide ("CO") emissions, SAI assumed that a 5/50 standard of 3.4 gpm would apply, followed by a 10/100 CO standard of 4.2 gpm.[1]

B.   The "Test" Fleet

None of the cars used in the test fleet has emission control

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[1]   These assumptions are generally consistent with provisions in both the Senate/Administration compromise bill (S.1630) and the bill approved by the House Energy & Commerce Committee (H.R. 3030).

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systems designed to meet the stricter emission standards noted above; automobile manufacturers design and build cars for certification under existing emission standards, not future standards.[2/] For this reason, the effort to determine the impact of the Additive on future emission standards required an initial judgment as to which of the existing emission control devices or systems in the test fleet best represents future emission control technology. In this regard, Ethyl assumed that those vehicle models which were able to meet, on average, the existing HC emission standard best represented the technology that will be used by automobile manufacturers to comply with future emission standards.

Ethyl decided to use the HC standard for this analysis since HC emissions were the only emissions for which the Additive had a slight, but statistically detectable, increase in Ethyl's durability test program. Applying this criteria, the models from Ethyl's test fleet included in this analysis are models C, E, G, H, and I.[3/]

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[2/] Since, by definition, emission control devices or systems designed to meet future emission standards do not yet exist, the legal standard under § 211(f) of the Act is only concerned with an additive's impact, if any, on the capability of the device or system to meet existing emission standards -- i.e., the standards under which the device or system has been certified.

[3/] Both the clear and Additive-fueled vehicles in Models D, F, and T exceeded the HC emission standard within the first 50,000 miles of vehicle operation, and were therefore excluded from further analysis in this Appendix. See Appendix 2A.

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III. SAI'S STATISTICAL ANALYSIS

Only three of the nine statistical tests used by EPA to determine the long-term deteriorative impact of an additive on tailpipe emissions consider specific emission standards. These tests are (1) the violation mileage test; (2) the maximum percentage of vehicles failing the standard test; and (3) the pivotal cause or contribute test.[4] Using the emission standards described above, SAI applied each of these three tests to the data for models C, E, G, H, and I.

SAI performed each of the three tests in three different ways -- 50,000 mile analysis based on linear regression, 50,000 mile analysis based on quadratic regression, and 75,000 mile analysis based on quadratic regression.[5] SAI also carried out the mean effects analysis described in Appendix 2A for the five models used in this analysis. The results of these analyses for NOx, CO, and HC emissions are provided in the tables in Attachment 11-1 and are summarized below.

A. NOx Emissions

Using the stricter NOx emission standards, no adverse effects are seen for any pollutant in any of the violation mileage or maximum percentage of vehicles failing the standard

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[4] Each of these tests is described in detail in Appendix 2A.

[5] The difference between the linear and quadratic regression analyses is described in detail in Appendix 2A.

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tests. In addition, the group of five models pass all cause or contribute tests. This implies that use of the Additive will not cause or contribute to the failure of emission devices or systems to meet the stricter NOx emission control standard currently under congressional consideration for application in the mid-1990's.

Indeed, SAI's mean effects analysis shows that while clear-fueled cars do not, on a weighted-average basis, meet either the 50,000 mile or 100,000 mile NOx standards, the cars using the HiTEC 3000 additive can meet these standards through 75,000 miles of vehicle operation.[6] This clearly demonstrates, as reflected in SAI's analysis in Appendix 2A, that the Additive has a beneficial effect on NOx tailpipe emissions, which will make it easier to achieve any stricter NOx emission standards likely to apply in the future.

B.   CO Emissions

As with the analysis for the NOx emissions, the CO emission data pass all of the tests noted above using both the 50,000 and 75,000 mile data sets, whether the tests are based on linear or quadratic regression. Unlike the NOx analysis, however, neither the clear-fueled vehicles nor the Additive-fueled vehicles meet,

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[6]   At the 50,000 mile emissions point, the clear-fuel cars averaged 0.44 gpm while the cars using the Additive averaged 0.33 gpm. At the 75,000 mile emissions point, the clear-fuel cars averaged 0.52 gpm while the cars using the Additive averaged 0.35 gpm. See Attachment 11-1.

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on a weighted-average basis, the 3.4 gpm CO emission standard
after 50,000 miles of vehicle operation, but the average
emissions of the Additive-fueled vehicles at 50,000 miles are
below those of the clear-fueled vehicles[7]. The mean effects
analysis also shows that both the clear-fueled and Additive-
fueled vehicles will meet the 4.2 gpm CO standard at 75,000
miles.[8]

Together, these results show that the Additive does not
adversely affect the capability of vehicles to meet the stricter
CO emission standards currently being considered by Congress.
While the test vehicles exhibit some difficulty meeting the
50,000 mile CO standard, SAI's analysis indicates that this
difficulty cannot be attributed to use of the Additive.

C. HC Emissions

No overall adverse effects are seen for HC emissions in any
of the violation mileage or maximum percentage of vehicles
passing the standard tests.[9] The HC emissions data for the five

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[7] At the 50,000 mile emissions point, CO emissions from clear-
fuel cars averaged 3.77 gpm, while the cars using the Additive
averaged 3.45 gpm. Id.

[8] Id.

[9] Because the proposed HC standard includes both a total HC
and a non-methane HC component, SAI calculated the methane/non-
methane breakdown for the HC emissions from the test fleet based
on special testing conducted on the test cars after 50,000 miles
of vehicle operation. This was the only mileage interval at
which Ethyl conducted such testing. By necessity, SAI assumed
(continued...)

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models also pass the pivotal cause or contribute tests. As with the NOx and CO analyses, these test results imply that the Additive will <u>not</u> cause or contribute to the failure to meet the stricter emission standards currently under consideration in Congress. Indeed, SAI's mean effects analysis shows that, regardless of the vehicle's fuel type, cars in models C, E, G, H, and I pass, on a weighted-average basis, the total HC standards applicable at 50,000 and 75,000 miles, as well as the corresponding non-methane HC standards.[10]

V. CONCLUSION

The analyses described above show that use of the HiTEC 3000 additive will <u>not</u> cause or contribute to the failure to meet the stricter emission standards currently being considered by Congress for application in the mid-1990's and beyond. Although this fact is not legally relevant to a decision on a waiver request under § 211(f)(4) of the Act, it is yet an additional consideration which supports prompt approval of Ethyl's waiver request for the HiTEC 3000 additive.

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[9] (...continued)
that the ratio of methane to non-methane components of the HC emissions at the 50,000 mile test interval applied to the HC emissions at all mileage intervals in the test program. <u>See</u> Attachment 11-1 (memorandum dated April 3, 1990).

[10] <u>Id.</u>

MEMORANDUM

TO: Ethyl Corporation HiTEC 3000 Team

FROM: Alison Pollack

DATE: 12 April 1990

SUBJECT: HiTEC 3000 Analyses related to Clean Air Act

We have completed the analyses for supporting Appendix 11 on Clean Air Act issues. This memo describes the results; the memo of 3 April 1990 (attached) describes details of the analyses performed. All relevant tables are enclosed.

Three of the EPA regression-based tests were carried out for each of the four pollutants (HC, NMHC, CO, and NO_x) of interest. These are the only EPA tests that consider specific standards -- the violation mileage test, the maximum percentage of vehicles failing the standard test, and the "pivotal" cause or contribute test. Each of these tests was performed in three different ways -- 50,000 mile analysis based on linear regression, 50,000 mile analysis based on quadratic regression, and 75,000 mile analysis based on quadratic regression.

No overall adverse effects are seen for any pollutant in any of the violation mileage or maximum percentage of vehicles failing standard tests. Overall, the group of five cars pass all cause or contribute tests.

In addition to the EPA tests, we also carried out a mean effects analysis; the tabular results are enclosed. Note that the average emissions reported are weighted averages across the five models. These weighted averages show that this group of models passes the 50K hydrocarbon standard of 0.31 g/mi and the 50K non-methane HC standard of 0.25 g/mi, no matter which fuel is used. Neither the clear- nor the HiTEC 3000-fueled cars, on average, pass the 50K carbon monoxide standard of 3.4 g/mi. The good news is that the clear-fueled cars, on average, do not pass the 50K NO_x standard of 0.4 g/mi, while the HiTEC 3000-fueled cars do.

The tables also show the 75,000 mile averages, which can be compared to the proposed 100K standards. The results are similar to the 50K results: both clear- and HiTEC-fueled cars are below the HC and NMHC standards and above the CO standards, and the clear-fueled cars are above the NO_x standard while the HiTEC-fueled cars are below.

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